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(54) PHOTSENSITIVE RESIN COMPOSITION, SCREEN PRINTING PLATE USING SAME AND METHOD FOR PRODUCING THE PLATE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a photosensitive resin composition excellent in water and organic solvent resistances and printing resistance and to produce a screen printing plate using the composition.

SOLUTION: A dispersoid comprising a water-insoluble or slightly water-soluble thermally crosslinkable compound is dispersed in a dispersion medium comprising a water-soluble saponified body of a vinyl acetate polymer containing a styrylpyridinium group or a styrylquinolium group and having  $\geq 50$  mol% saponification degree to obtain the objective photosensitive resin composition. The objective screen printing plate has a resin layer comprising the photosensitive resin composition in which water-insoluble particles, hydrophobic polymer particles and the saponified body have been crosslinked and integrated. The photosensitive resin composition is applied to a screen mesh, dried, exposed, developed and heated or irradiated with thermic rays to produce the screen printing plate.

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(54) 【発明の名称】 感光性樹脂組成物及びそれを用いたスクリーン印刷用版並びにスクリーン印刷用版の製造方法

(57) 【要約】 (修正有)

【課題】 耐水性、有機溶剤性、耐刷性に優れた、感光性樹脂組成物及びそれを用いたスクリーン印刷用版並びにスクリーン印刷用版の製造方法を提供する。

【解決手段】 スチリルビリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に、水不溶性又は難溶性の熱により架橋する架橋性化合物からなる分散質を分散してなることを特徴とする感光性樹脂組成物。及び、該感光性樹脂組成物からなる樹脂層において、該水不溶性粒子と疎水性重合体粒子と酢酸ビニル重合体鹼化物とが架橋して一体化されている、スクリーン印刷用版。及び、該感光性樹脂組成物を、スクリーンメッシュに塗布し、乾燥させた後、露光し、現像した後で、加熱又は熱線を照射することを特徴とするスクリーン印刷用版の製造方法。

## 【特許請求の範囲】

【請求項1】スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に、水不溶性又は難溶性の熱により架橋する架橋性化合物からなる分散質を分散してなることを特徴とする感光性樹脂組成物。

【請求項2】疎水性重合体粒子が分散質として分散されている、請求項1に記載の感光性樹脂組成物。

【請求項3】光重合可能なエチレン性不飽和基を有する化合物に光重合開始剤を溶解又は混合したものが分散質として分散されている、請求項1又は2に記載の感光性樹脂組成物。

【請求項4】水性分散媒中にジアゾ樹脂が含有されている、請求項1～3のいずれかに記載の感光性樹脂組成物。

【請求項5】熱により架橋する架橋性化合物がブロックイソシアネート化合物である、請求項1～4のいずれかに記載の感光性樹脂組成物。

【請求項6】スクリーンメッシュに部分的に樹脂層を形成してなり、該樹脂層が、光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物中に熱により架橋された水不溶性粒子が分散されたものからなり、且つ、該熱により架橋された水不溶性粒子と光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物とが架橋して一体化されていることを特徴とするスクリーン印刷用版。

【請求項7】樹脂層が、光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物中に熱により架橋された水不溶性粒子と疎水性重合体粒子とが分散されたものからなり、且つ、該熱により架橋された水不溶性粒子と疎水性重合体粒子と光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物とが架橋して一体化されている、請求項6に記載のスクリーン印刷用版。

【請求項8】スクリーンメッシュが、筒状のロータリースクリーンシリンダーである、請求項6又は7に記載のスクリーン印刷用版。

【請求項9】スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に、水不溶性又は難溶性の熱により架橋する架橋性化合物からなる分散質を分散してなる感光性樹脂組成物を、スクリーンメッシュに塗布し、乾燥させた後、露光し、現像した後、加熱又は熱線を照射することを特徴とするスクリーン印刷用版の製造方法。

【請求項10】感光性樹脂組成物中に疎水性重合体粒子が分散質として分散されている、請求項9に記載のスクリーン印刷用版の製造方法。

【請求項11】感光性樹脂組成物の分散媒中にジアゾ樹脂が含有されている、請求項8又は9に記載のスクリーン印刷用版の製造方法。

【請求項12】熱により架橋する架橋性化合物がブロックイソシアネート化合物である、請求項9～11のいずれかに記載のスクリーン印刷用版の製造方法。

【請求項13】スクリーンメッシュが、筒状のロータリースクリーンシリンダーである、請求項9～12のいずれかに記載のスクリーン印刷用版の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、耐水性、有機溶剤性、耐刷性に優れた各種印刷用版を製造することができる感光性樹脂組成物及びそれを用いたスクリーン印刷用版並びにスクリーン印刷用版の製造方法に関し、特にロータリースクリーンに適した感光性樹脂組成物及びそれを用いたスクリーン印刷用版並びにスクリーン印刷用版の製造方法に関するものである。

## 【0002】

【従来の技術】従来、水現像可能な感光性材料として、多数の感光性樹脂材料が提案されてきた。しかしながら、水現像可能な感光性樹脂材料として用いられる基材樹脂は、親水性基を備えた水溶性の樹脂が用いられるために、十分な耐水性を備えた硬化画像が得られる感光性樹脂材料とならなかった。特に、水現像可能な感光性樹脂材料中には、水現像性を良好なものとするために、水溶性の化合物や界面活性剤、或いは、親水性基を持つ自己乳化可能な化合物等が用いられている。その結果、現像の光硬化後においても親水性基が残り、十分な耐水性を持たせることはできなかった。また、捺染用に用いる場合には、捺染糊に含まれる顔料や染料の画像への染み込みが生じたり、反応性染料を使用する場合には、画像を構成する水溶性ポリマーの水酸基と反応性染料との反応による画像の汚染が生じるため、綺麗な染色を行ない難い等の問題を解消することが難しかった。この様な欠点を改善するために、従来から硬化特性や耐水性の良い硬化剤として重クロム酸塩類が多用されてきた。

## 【0003】

【発明が解決しようとする課題】しかし、重クロム酸塩類を用いた感光液や感光膜は、6価クロムに毒性があり、工業的に使用するためには、製版時の排水や使用済みの製品の回収等の環境破壊を十分に配慮して実施しなければならないために、事実上工業的な実施が難しいのが現状である。けれども、ロータリースクリーンを用いた捺染においては、その装置の性能上から、一段と優れた耐水性及び耐溶剤性が要求されるため、現在でもポリ酢酸ビニルの鹼化物、ポリ酢酸ビニルエマルジョン及び重クロム酸塩からなる感光性樹脂組成物が用いられている。

【0004】一方、ジアゾ樹脂を用いた感光液や感光膜は、上記重クロム酸塩類と同様に良好な耐水性及び耐溶剤性を示すものが得られるが、ジアゾ樹脂を感光液に添加した感光液や感光膜は経時変化が大きく、安定した品

質の硬化画像が得られ難いことから、感光液をスクリーンメッシュに塗布する直前にジアゾ樹脂を感光液に添加しなければならなかった。例えば、ジアゾ樹脂と感光液とを混合したものは、1週間で画像に影響を及ぼすこととなる。また、ジアゾ樹脂と感光液との混合物を塗布後に乾燥させたものは、暗反応が起こるために、露光させなくても2〜3週間で架橋反応が生じて画像に影響がある。従って、感光液をスクリーンメッシュに塗布する毎に、感光液に一定割合のジアゾ樹脂を調合して添加しなければならぬため、製膜に時間がかかり作業性に劣る等の欠点を有していた。更に、より一層改良された耐水性に優れる水現像可能な感光性樹脂組成物が求められている。また、一般印刷に多用されているフラットスクリーン印刷においても、安全性や脱環境破壊の趨勢から、印刷時に用いられるインキとして水性インキが使用される傾向にあり、より一層の耐水性及び耐溶剤性に優れた感光液や感光膜が求められるようになった。

#### 【0005】

【課題を解決するための手段】本発明者は、上記問題点に鑑みて鋭意研究を重ねた結果、耐水性、有機溶剤性、耐刷性に優れたスクリーン印刷用版を得るためには、安全性や脱環境破壊の趨勢から、それ自体で光架橋性を有する光架橋性基を含有する水可溶性の鹼化度50〜99モル%の部分鹼化酢酸ビニル重合体からなる分散媒を露光・現像させた後に、分散質として含有する水不溶性又は難溶性の架橋性化合物を熱により架橋させることにより、光架橋した水に難溶性の鹼化度50〜99モル%の部分鹼化酢酸ビニル重合体中に残存する親水性基を減少させて、分散媒をより一層水に不溶化することにより、耐水性、有機溶剤性、耐刷性に優れたスクリーン印刷用版が得られるとの知見に基づき本発明を完成するに至ったものである。

【0006】すなわち、本発明の感光性樹脂組成物は、スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に、水不溶性又は難溶性の熱により架橋する架橋性化合物からなる分散質を分散してなること、を特徴とするものである。本発明のもう一つの発明であるスクリーン印刷用版は、スクリーンメッシュに部分的に樹脂層を形成してなり、該樹脂層が、光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物中に熱により架橋された水不溶性粒子が分散されたものからなり、且つ、該熱により架橋された水不溶性粒子と光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物とが架橋して一体化されていること、を特徴とするものである。本発明の更なるもう一つの発明であるスクリーン印刷用版の製造方法は、スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に、水不溶性又は難溶性の熱により架橋する

架橋性化合物からなる分散質を分散してなる感光性樹脂組成物を、スクリーンメッシュに塗布し、乾燥させた後、露光し、現像した後で、加熱又は放射線を照射すること、を特徴とするものである。

#### 【0007】

【発明の実施の形態】[1] 感光性樹脂組成物

##### (1) 構成成分

##### (A) 分散媒

本発明の感光性樹脂組成物において分散媒成分として用いられる、スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物としては、水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物に側鎖としてスチリルピリジニウム基(化1)或いはスチリルキノリウム基(化2)を付加させたものである。

##### 【0008】(a) 酢酸ビニル重合体鹼化物

上記鹼化度50モル%以上の酢酸ビニル重合体鹼化物としては、一般に酢酸ビニル重合体を50モル%以上の割合で鹼化することにより得られる鹼化度50モル%以上の酢酸ビニル重合体鹼化物であり、鹼化度を100モル%とすることによりポリビニルアルコールが得られる。本発明の鹼化度50モル%以上の酢酸ビニル重合体鹼化物の中には鹼化度100モル%のポリビニルアルコールも包含されるものである。

##### 【0009】酢酸ビニル重合体

上記鹼化度50モル%以上の酢酸ビニル重合体鹼化物に用いられる酢酸ビニル重合体としては、酢酸ビニルのホモ重合体及び共重合体のいずれをも含むものである。具体的には、ポリ酢酸ビニル、酢酸ビニルとこれと共重合可能な単量体(共単量体)との共重合体である。酢酸ビニルと共重合可能な単量体としては、例えば、エチレン又はエチレン性不飽和基を持つ化合物、具体的には、アクリル酸、メタクリル酸、クロトン酸、マレイン酸、フマル酸、イタコン酸等の不飽和カルボン酸類、メチルアクリレート、メチルメタクリレート、2-エチルヘキシルアクリレート、ブチルアクリレート等のアクリレート類；アクリルアミド、メタクリルアミド、N-メチロールアクリルアミド、N,N-ジメチルアクリルアミド等のアクリルアミド類；塩化ビニル、プロピレン、ブチレン、スチレン等のビニル化合物；ジメチルアミノエチルメタクリレート、ビニルイミダゾール、ビニルピリジン、ビニルサキシミド等のカチオン性モノマー類等を挙げることができる。これらの化合物は単独または併用して使用することもでき、上記重合体中の含有量は30mol%以下が好ましい。

##### 【0010】鹼化度

上記鹼化度50モル%以上の酢酸ビニル重合体鹼化物としては、酢酸ビニル重合体を部分鹼化させて鹼化度50モル%以上の、好ましくは50〜100モル%、特に好ましくは70〜99モル%とした水可溶性の酢酸ビニル

重合体鹼化物とすることができる。そして、「鹼化度50モル%以上」とは、この酢酸ビニル重合体が酢酸ビニルのホモ重合体であるとき、ビニルアルコール部分の含量が50モル%以上の部分鹼化酢酸ビニル重合体鹼化物であることを意味する。

#### 【0011】重合度

上述の鹼化度50モル%以上の酢酸ビニル重合体鹼化物は、水現像可能でかつ光硬化後に耐溶剤性及び耐水性に優れた硬化膜を得ることのできる組成物を与えるためである。また、同様の理由でその重合体の重合度は、一般に300~5,000のもの、好ましくは500~3,500のものをを用いることが望ましい。

【0012】本発明の感光性樹脂組成物において分散媒成分として用いられる、スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物は、水可溶性で、且つ、水不溶性又は難溶性の熱により架橋する架橋性化合物よりなる分散質、必要により用いられる疎水性重合体粒子よりなる分散質を乳化特性或いは保護コロイド特性を持ち、通常の条件下では一般有機溶媒には溶解しない特性が必要である。従って、酢酸ビニル重合体の鹼化物（鹼化度50モル%以上）、或いは、酢酸ビニルとエチレン又はエチレン性不飽和基を持つ化合物との共重合物の鹼化物（鹼化度50モル%以上）又はポリビニルアルコール重合体、或いはこれらの誘導体が適当である。ま\*

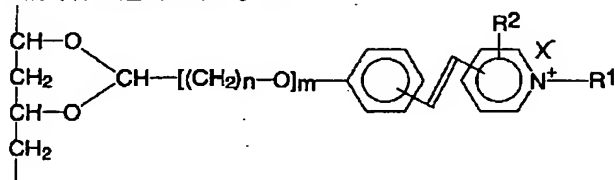
\*た、重合体鹼化物の誘導体としては、ホルムアルデヒド、アセトアルデヒド、ブチルアルデヒド、ベンズアルデヒド等を付加した物を使用できる。その付加量は30mol%以下が好ましい。具体的には、鹼化ポリ酢酸ビニルのホルマール化又はブチラール化等の低級（C<sub>1</sub>~C<sub>4</sub>）アセタール化物及びp-ベンズアルデヒドスルホン酸、β-ブチルアルデヒドスルホン酸、o-ベンズアルデヒドスルホン酸、2,4-ベンズアルデヒドジスルホン酸等によるアセタール化物を含み、かつこれらの側鎖誘導体を挙げるることができる。

#### 【0013】(b) 光架橋性基

本発明の感光性樹脂組成物において水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物中に側鎖として含有されるスチリルピリジニウム基（化1）又はスチリルキノリウム基（化2）としては、それ自体で光架橋性を有する光架橋性基である。本発明において用いられるスチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物は、下記一般式（I）及び（II）で表わされるスチリルピリジニウム基（化1）或いはスチリルキノリウム基（化2）を付加させたものである。一般式（I）

#### 【0014】

#### 【化1】

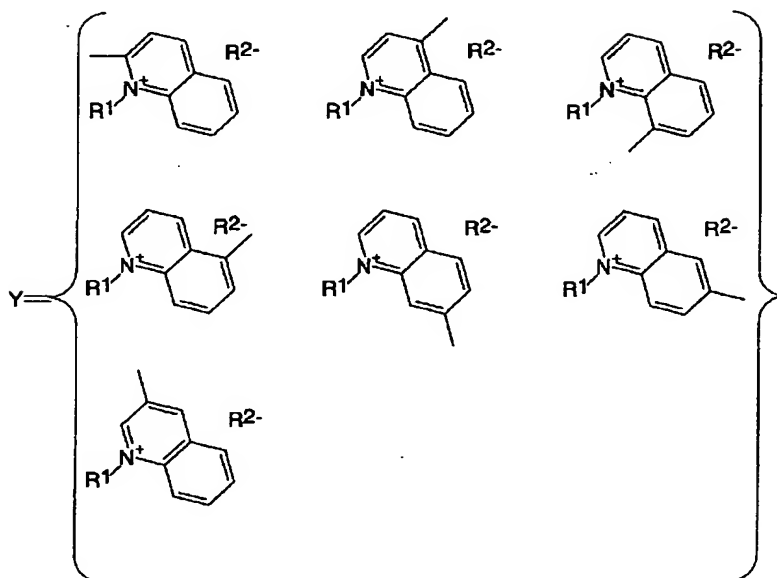
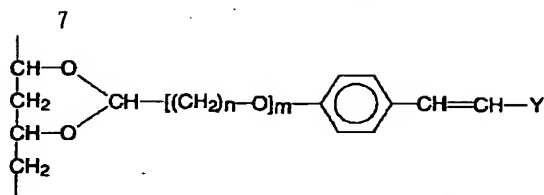


#### 【0015】(化1)

一般式 (II)

#### 【0016】

#### 【化2】



## 【0017】(化2)

但し、上記一般式(I)及び(II)中、 $R^1$ は水素原子、アルキル基、又はアラルキル基を示し、これらはヒドロキシ基、カルバモイル基、エーテル結合、不飽和結合を含んでも良く、 $R^2$ は水素原子又は低級アルキル基を示す。 $X^-$ はハロゲンイオン、リン酸イオン、 $p$ -トルエンスルホン酸イオン又はこれら陰イオンの混合物を示し、 $m$ は0又は1、 $n$ は1~6の整数を示す。上記のようなスチルバゾリウム基を有する部分鹼化酢酸ビニル重合体及びその製造法は既に知られている(特開昭55-23163号、特開昭55-62905号、特開昭55-62405号各公報)。光二量化反応性のスチリルピリジニウム基及びスチリルキノリニウム基の付加量は、一般に0.2~7.0モル%、好ましくは0.5~5.0モル%である。上記範囲未満であると画像形成が十分にできない傾向がある。また、上記範囲を超過すると水溶解性が悪くなる傾向がある。これらスチリルピリジニウム基又はスチリルキノリニウム基を含有する水溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒成分は、水により希釈されているのが普通である。

## 【0018】(B) 水不溶性又は難溶性の架橋性化合物(分散質)

## (a) 架橋性化合物

本発明の感光性樹脂組成物において分散質成分として用いられる、水不溶性又は難溶性の架橋性化合物よりなる分散質としては、熱により架橋する架橋性化合物である。熱により架橋する架橋性化合物としては、加熱或いは熱線を照射することにより分散媒成分として用いられている鹼化度50モル%以上の酢酸ビニル重合体又はポリビニルアルコール重合体の水溶性-OH基や-COOH基及び-NH<sub>2</sub>、-SH等の活性水素を持つ基と反応することができる官能基を有する化合物、好ましくは2個以上の官能基を有する化合物である。この様な官能基の具体例としては、例えば、アルデヒド基、イソシアネート基、アルコキシ基、グリシジル基、エチレン性不飽和基、アミノ基、ジエステル類等を挙げることができる。この様な官能基を有する化合物としては、具体的には、例えば、チオ尿素、メラミン、ベンゾグアミン等のアミノ化合物、メチロール化メラミン、ブチロール化メラミン、メチロールアクリルアミド等のアルコキシ化合物、グリオキザール、グルタルアルデヒド等のジアルデヒド化合物、下記に示すブロックイソシアネート化合物、コバルト、チタン、ジルコニウム、モリブデン等の金属キレート化合物、アクリロイル基、メタアクリロイル基、Sクリルアミド基、ビニルエーテル基等のエチレ

ン性不飽和基含有化合物等を挙げることができる。更に、これらの化合物を共存させることで、より効果的に使用できる。これら官能基を有する化合物の中でも、特にブロックイソシアネート化合物を用いた感光性樹脂組成物は長期安定性に優れていることから好ましい。

#### 【0019】ブロックイソシアネート化合物

上記ブロックイソシアネート化合物は、イソシアネート化合物のイソシアネート基をブロック剤（例えば、活性水素を有するカプロラクタム、活性メチレン、オキシム等の化合物）によりマスクしたものであり、常温では安定であるが加熱（通常120℃以上）するとブロック剤が解離して活性なイソシアネート基が再生されるものである。上記ブロックイソシアネート化合物に用いられるイソシアネート化合物としては、イソシアネート基が2個以上有するもので、この様な化合物の具体例としては、2, 6-トリレンジイソシアネート（2, 6-トリレンジイソシアネート）、2, 4-トリレンジイソシアネート（2, 4-トリレンジイソシアネート）、4, 4-ジフェニールメタンジイソシアネート、1, 5-ナフタレンジイソシアネート、m-キシレンジイソシアネート、m-テトラメチルキシレンジイソシアネート等の芳香族ジイソシアネート、メチルヘキサメチレンジイソシアネート、2, 2, 4-トリメチルヘキサメチレンジイソシアネート、2, 4, 4-トリメチルヘキサメチレンジイソシアネート等の脂肪族イソシアネート、イソホロンジイソシアネート、水素添加4, 4'-ジフェニールメタンジイソシアネート、水素添加m-キシレンジイソシアネート等の脂環族ジイソシアネート、トリフェニールメタントリイソシアネート、ポリメチレンポリフェニルイソシアネート、トリレンジイソシアネートのトリメチロールプロパンアダクト体やイソシアヌレート体、ポリメリックメタンジイソシアネート、その他プレポリマーイソシアネート類等の多官能芳香族イソシアネート化合物等を挙げることができる。これらのイソシアネート化合物にブロック剤でマスクしたブロックイソシアネート化合物は単独或いは併用して用いることができる。上記ブロックイソシアネート化合物は、感光性樹脂組成物中のスチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒成分中に乳化分散して微細に分散した乳化ブロックイソシアネート化合物であることが好ましい。その結果、安定した感光性樹脂組成物が得られる。また、単独では乳化しない化合物でも、他の化合物と混合して乳化させても良く、更に、有機溶媒（疎水性が好ましい）に溶解して使用しても良い。分散媒成分中に、乳化・分散したブロックイソシアネート化合物には、相溶するポリマーやプレポリマーを混合して使用しても良く、この様なポリマーやプレポリマーは、必ずしも-OH基や-COOH基及び-NH<sub>2</sub>基、-SH基等を持ち、イソシアネート基と反応性に富んだ化合物であ

る必要はない。但し、水に難溶性で、乳化・分散特性の良いものが好ましい。

#### 【0020】(b) 分散質成分の水不溶性又は難溶性

本発明の感光性樹脂組成物において分散質成分として用いられる、水不溶性又は難溶性の熱により架橋する架橋性化合物は、本発明の感光性樹脂組成物中に含まれる、スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に分散されなければならないことから、水不溶性又は難溶性のものであることが重要である。また、水不溶性又は難溶性の熱により架橋する架橋性化合物よりなる分散質は、先ず、露光工程で感光性樹脂組成物をマスクフィルムを介して露光させることにより感光性樹脂組成物中の分散媒成分を光硬化させ、更に、水現像することによって未露光の分散媒成分を溶解除去して画像を形成させた後に、加熱又は熱線照射工程で分散質成分に加熱或いは熱線を照射することにより分散質成分を硬化させるために、前工程である画像形成時の現像工程において分散質成分が水により溶解して抽出されないことが重要である。

#### 【0021】架橋

この様な分散質として上記官能基を有する架橋性化合物を用いることにより、分散媒成分の光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物中に残存するOH基等の親水性基と結合して親水性基を減少させることによって更に水に不溶性にすると共に、光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物と架橋して一体化され、より一層不溶化させることができるため、得られるスクリーン印刷用版の画像を形成した感光樹脂層は、より一層耐水性、有機溶剤性、耐刷性を向上させることができる。

#### 【0022】(c) 配合割合

本発明の感光性樹脂組成物中に含有されるスチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒と、該分散媒中に分散される水不溶性又は難溶性の熱により架橋する架橋性化合物よりなる分散質との配合割合は、水性分散媒中の固形分100重量部に対して、架橋性化合物を一般に10~500重量部、好ましくは30~400重量部、特に好ましくは50~300重量部の割合で配合される。上記範囲未満では耐水・耐溶剤性の改善に効果が十分でない傾向がある。また、上記範囲を超過すると乳化安定性が悪く分離析出し易くなる傾向がある。更に、コーティングし、乾燥後の感光樹脂膜はタックが強く、架橋性化合物のブリードが激しくなる傾向がある。

#### 【0023】(2) 任意の構成成分

本発明の感光性樹脂組成物は、基本的には上記構成成分よりなるが、任意の成分として以下に示す疎水性重合体粒子、光架橋剤、光重合開始剤を含有するエチレン性不

飽和基を有する化合物を配合することが好ましい。

【0024】(A) 疎水性重合体粒子

上記感光性樹脂組成物中に疎水性重合体粒子よりなる分散質を含有させることにより一層耐水性を向上させることができる。水不溶性高分子分散物は、重合工程により得られるエマルジョンをそのまま、或いは、高分子重合体を水及び水を主たる分散媒に分散された高分子重合体の分散液が用いられる。この様な疎水性重合体粒子を含有する高分子重合体の分散液は、スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に容易に混合でき、凝集や沈殿を起こさないものであれば使用することができる。この様な疎水性重合体粒子が分散された感光性樹脂組成物は、疎水性重合体粒子の平均粒子径が50 $\mu$ m以下、特に15 $\mu$ m以下であることが好ましい。この様な疎水性重合体粒子成分の配合量は、感光性樹脂組成物中の固形分100重量部に対して、固形分として5~95重量部、好ましくは20~85重量部とすることが望ましい。疎水性重合体粒子成分の配合量が上記範囲未満では硬化膜への耐水性向上効果が現れ難い傾向があり、上記範囲を超過すると現像性が悪く再現性の良い画像が得られ難い傾向がある。この様な疎水性重合体粒子成分は、重合工程により得られるエマルジョンをそのまま、或いは、高分子重合体を水及び水を主たる分散媒に分散された高分子重合体の分散液が用いられる。これらの疎水性重合体粒子成分は、合成された高分子化合物及び天然高分子化合物でも良い。本発明の疎水性重合体粒子成分の効果は、形成された画像の耐水性を改善し、その結果として、光硬化画像の解像性の向上と、水性インキや水性ペーストを用いた印刷での耐刷性向上関係する。

【0025】上記疎水性重合体粒子としては、例えば、ポリ酢酸ビニル、酢酸ビニル/エチレン共重合体、酢酸ビニル/アクリル酸エステル共重合体（ここでアクリル酸エステルとしては、例えば、アクリル酸メチル、アクリル酸2-エチルヘキシル等がある。）、（メタ）アクリル酸重合体、スチレン/ブタジエン共重合体、メタクリル酸メチル/ブタジエン共重合体、アクリロニトリル/ブタジエン共重合体、クロロプレン重合体、イソプレン重合体、ポリ塩化ビニル、ポリ塩化ビニリデン、ポリスチレン、シリコーン樹脂、ポリエチレン、ポリウレタン、フッ素樹脂等を挙げることができる。これら疎水性重合体粒子は、重合工程により得られるポリ酢酸ビニルエマルジョン、エチレン・酢酸ビニルコポリマーエマルジョン、酢酸ビニル・アクリルコポリマーエマルジョン、エチレン・酢酸ビニル・アクリル3元共重合エマルジョン、塩化ビニル・酢酸ビニルエマルジョン、アクリルエマルジョン、スチレン・ブタジエンラテックスエマルジョン、MBRラテックスエマルジョン、アクリロニトリル・ブタジエンゴムラテックスエマルジョン、クロ

ロブレンゴムラテックスエマルジョン、塩化ビニリデンエマルジョン等を挙げることができる。合成高分子ディスパーションとしては、ポリエチレンジスパーション、ポリオレフィンアイオノマーディスパーション、ウレタンアイオノマーディスパーション等が有用である。また、合成高分子微粉体や精製スターチを分散したものも使用できる。

【0026】(B) 光架橋剤

本発明の感光性樹脂組成物は、水性分散媒成分中に含まれる光架橋性を有する光架橋性基により十分な硬化画像を得ることができるが、更に、光架橋剤（ジアゾ樹脂）を添加することによりより一層優れた硬化画像を得ることができる。但し、光架橋剤のみを添加する場合には感光性樹脂組成物の保存安定性が悪化したり、光感度が低下する欠点もある。この様なジアゾ樹脂化合物としては、p-ジアゾフェニルアミンのパラフォルムアルデヒド縮合物または4, 4'-ジメトキシジフェニルエーテル縮合物、4-ジアゾ3-メトキシジフェニルアミンのパラフォルムアルデヒド縮合物、または4, 4'-ジメトキシジフェニルエーテル縮合物等を挙げることができる。更に、特開平5-125031号公報に記載の新規ジアゾ化合物等も有用である。ジアゾ樹脂を含有させる場合には、感光性樹脂組成物中の固形分100重量部に対して、固形分として0.1~4重量部、好ましくは0.2~2.5重量部の割合で含有されていることが望ましい。

【0027】(C) 光重合開始剤を含有するエチレン性不飽和基を有する化合物

エチレン性不飽和基を持つ化合物に光重合開始剤を溶解または混合して使用すると、この混合物は光により重合して高分子化する。また、同時に水性分散媒成分及び分散質とグラフト重合架橋もおこり、硬化物の耐水・耐溶剤性を向上させる。エチレン性不飽和基を持つ化合物としては水に不溶で成分(A)溶液に容易に乳化できるものが好ましい。

【0028】エチレン性不飽和基を有する化合物

この様なエチレン性不飽和基を有する化合物としては、アクリロイル基、メタアクリロイル基、アリル基、ビニルエーテル基、アクリルアミド基、メタアクリルアミド基等のエチレン性不飽和基を1個以上有するもので、水に不溶性或いは難溶性のものが好ましく、特に好ましくはアクリロイル基、メタアクリロイル基を1個以上有する化合物である。この様な化合物としては、具体的には、例えば、ペンタエリスリトールトリ（メタ）アクリレート、ペンタエリスリトールテトラ（メタ）アクリレート、トリメチロールプロパントリ（メタ）アクリレート、トリメチロールエタントリ（メタ）アクリレート、ジペンタエリスリトールヘキサ（メタ）アクリレート、エチレングリコールジ（メタ）アクリレート、ジエチレングリコールジ（メタ）アクリレート、テトラエチレン



グリコールジ(メタ)アクリレート、ヘキサエチレングリコールジ(メタ)アクリレート、ジブロムヘオペンチルグリコールジ(メタ)アクリレート、2,8ジブロムネオペンチルグリコールジ(メタ)アクリレート等のタカアルコール多価アクリレート類、2,2-ビス(4-メタクリロキシエトキシフェニル)プロパン、2,2-(4-アクリロキシエトキシフェニル)プロパン、ビスフェノールA、エピクロルヒドリン系のエポキシ樹脂のアクリル酸又はメタクリル酸付加物等のエポキシアクリレート、トリメチロールプロパントリグリシジルエーテルのアクリル酸又はメタアクリル酸との付加物、トリヘキサメチレンジイソシネートと2価アルコールの(メタ)アクリルモノ酸エステルとの反応で得られるウレタン(メタ)アクリル化合物等が挙げられる。これらの化合物は単独或いは2種以上を併用して用いることができる。このような光重合開始剤を含有するエチレン性不飽和基を有する化合物が分散された感光性樹脂組成物は、エチレン性不飽和基を有する化合物の平均粒子径が $20\mu\text{m}$ 以下、特に $10\mu\text{m}$ 以下であることが好ましい。この様なエチレン性不飽和基を有する化合物成分の配合量は、感光性樹脂組成物中の固形分100重量部に対して、0.5~70重量部、好ましくは1~50重量部とすることが望ましい。エチレン性不飽和基を有する化合物成分の配合量が上記範囲未満では現像時の耐水性向上効果が現れ難い傾向があり、上記範囲を超過すると現像性が悪く再現性の良い画像が得られ難い傾向がある。

#### 【0029】光重合開始剤

上記重合性化合物を光照射により速やかに反応させるためには、光重合開始剤を添加することが一般的である。この様な光重合開始剤は上記重合性化合物に溶解あるいは相溶し、均一に混合される事が好ましい。この様な光重合性開始剤としてはベンゾフェノン、ベンゾインアルキルエーテル、ミヒラーズケトン、ベンジル、ベンジルジアルキルエーテル、ターシャールブチルアントラキノン等のアントラキノン類、クロロチオキサントン、イソプロピルチオキサントン等のチオキサントン誘導体等が挙げられる。更に、p-ジメチルアミノ安息香酸イソアミルエステル、p-ジメチルアミノ安息香酸エチルエステル等の光重合促進剤を混合しても良い。これらは、ベンゾフェノン系やチオキサントン系を用いた場合の重合硬化速度を速める上で効果的である。上記光重合性開始剤は、エチレン性不飽和基を有する化合物100重量部に対して、一般に1~10重量部の割合で配合される。

#### 【0030】(D) その他の任意成分

本発明の感光性樹脂組成物は、上記任意成分が配合されることが好ましいが、更に、この種の感光性樹脂組成物に通常含まれる添加剤成分を任意に添加することができる。この様な任意の添加剤成分としては、例えば、上記感光性樹脂組成物中の固形分100重量部に対して0.5重量部以下の乳化安定剤を、熱により架橋する架橋性

化合物や光重合可能なエチレン性不飽和基を含有する化合物の溶解補助剤として、それら100重量部に対して30重量部以下の水と混和性のない有機溶剤を、更には、染料、顔料等の画像を見易くする着色剤、消泡剤等を通常添加される範囲内で添加することができる。また、増量剤或いはタック防止剤として無機粉体を感光性樹脂組成物中の固形分100重量部に対して30重量部以下の範囲内で添加することができる。

#### 【0031】(3) 感光性樹脂組成物の調製

上記構成成分及び任意成分から本発明の感光性樹脂組成物を得るには、通常、以下に示す方法により調製することができる。

#### 感光性重合体の製造

部分酸化する酢酸ビニル重合体を水に溶解し、この溶液にスチリルピリジニウム基又はスチリルキノリウム基を含有する化合物を溶解し、更にリン酸を添加して反応させる。この反応液を陰イオン換樹脂を充填したカラムに通し、薄黄色の粘調液よりなるスチリルピリジニウム基又はスチリルキノリウム基が付加した部分酸化ポリ酢酸ビニル重合体よりなる感光性重合体水溶液が得られる。

#### 【0032】乳 化

この感光性重合体水溶液に、熱により架橋する架橋性化合物、或いは、必要に応じて用いる少量の有機溶剤を混合した熱により架橋する架橋性化合物を添加して、ニーダーやホモミキサー・スクリュウ式攪拌機等で攪拌して乳化することにより、本発明の感光性樹脂組成物が得られる。

#### 【0033】任意成分の配合

更に、必要に応じて光重合開始剤や光重合促進剤を溶解混合した光重合性化合物を添加して乳化したり、また、必要に応じて疎水性高分子重合体分散液や着色剤・消泡剤を混合したり、必要に応じて、光架橋剤であるジアゾ化合物を添加して混合することにより、更に改良された本発明の感光性樹脂組成物が得られる。尚、各成分の添加順序は上記順番に固定されるものでなく、凝集・分離・析出等の混合時の問題が生じない範囲で添加順序を変更することができる。但し、ジアゾ化合物は水溶液中での安定性が良くないために、感光液の保存安定性が低下し易い。従って、使用直前に添加することが好ましい。

#### 【0034】(4) 用 途

この様な本発明の感光性樹脂組成物は、各種用途に応じて、アルミニウム、ニッケル、ステンレス等の金属板や、合成樹脂板、半導体基板、石材等の任意の基材上に塗布し、乾燥して積層するか、各種スクリーンメッシュ(ポリアミド、ポリエステル、ステンレス等のメッシュ)、ロータリースクリーンシリンダー等の表裏面又は表面に塗布し、乾燥することにより形成された、例えば1~1000 $\mu\text{m}$ の乾燥厚の感光性樹脂材料に、紫外線等からなる活性光を、例えば、紫外線の場合には波長300~450nm範囲の照射エネルギー量が10mJ/

$\text{cm}^2$  以上となるようにマスク等により所定のパターンを通して照射して照射部分を硬化させた後、非照射部分の未硬化の部分をスプレー水等により除去すれば、レリーフ画像或いは画像膜が形成される。更に、この形成されたレリーフ画像或いは画像膜を50～220℃、好ましくは120～200℃の雰囲気中で加熱処理、或いは、近赤外線、遠赤外線、マイクロ波等を照射処理することにより、更に画像膜の硬化反応が進行し、耐水・耐溶剤性に優れた画像膜となる。従って、このような感光性樹脂組成物を使用したスクリーン印刷や凸版印刷等の各種印刷版や、各種エッチングレジスト、サンドブラストエッチング等のレジスト膜等の用途に利用することができる。これら用途の中でもスクリーン印刷用版として用いることが好ましい。

#### 【0035】[1] スクリーン印刷用版の製造

上記の様に得られた感光性樹脂組成物の好ましい用途としてのスクリーン印刷用版の製造方法について、以下に詳細に記載する。

##### (1) 塗布・乾燥工程

用途に応じて、アルミニウム、ステンレス、鋼鉄等の金属製の棒状素材を正方形或いは長方形に製作したフラットスクリーン型枠に、各種スクリーンメッシュで紗張りしたフラットスクリーン版に、フラットスクリーン版用バケットで、常法に従って上記感光性樹脂組成物を塗布及び乾燥工程を繰り返し、所定の厚みで積層するか、或いは、エレクトロフォーミング法により形成された金属製のロータリースクリーンシリンダー上に、リング状バケットで、常法に従って上記感光性樹脂組成物の塗布及び乾燥工程を1回又は数回繰り返すことにより、乾燥膜厚が一般に0.5～1.000 $\mu\text{m}$ 、好ましくは1～400 $\mu\text{m}$ 、特に好ましくは1～200 $\mu\text{m}$ の厚さの感光性樹脂組成物よりなる感光性樹脂膜が形成される。このようにして得られた感光性樹脂組成物よりなる感光性樹脂膜の表裏両面へは、該感光膜保護のためにオーバーコート層を形成することもできる。これによってスクリーン印刷用PS版を得ることができる。スクリーン印刷用版を得るに際して、感光液を直接塗布する方法と感光液をポリエチレン、ポリ塩化ビニル、ポリエステル等のプラスチックフィルム上に塗布・乾燥して5～1.000 $\mu\text{m}$ の感光膜を得ておいて、この感光膜を、水或いは感光液を塗布したスクリーン上に転写する方法（いわゆる直間法と呼ばれる方法）がある。本発明の感光性樹脂組成物はこのような方法で感光膜を形成することができる。

##### 【0036】(2) 露光工程

上記型枠に張られたスクリーンに感光性樹脂組成物よりなる感光膜をネガフィルム又はポジフィルムよりなるフィルムを介して紫外線、可視光線、アルゴンレーザー等の光線を照射して露光することにより、該フィルムに画像が描かれていて光を透過しない部分の裏面側の感光性

樹脂層中のスチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒が未露光となり硬化しない。一方、該フィルムに画像が描かれていない部分の裏面側の感光性樹脂層中のスチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒が露光されて光反応を起こし光架橋することにより硬化して、この部分の感光性樹脂層に潜像画像を形成させることができる。露光は、一般に出力1～15KW、好ましくは2～6KWの超高圧水銀灯、高圧水銀灯、メタルハライド含有高圧水銀灯等の光源を使用でき、一般に0.1～2m、好ましくは0.2～1.5mの距離から、一般に3秒～20分間、好ましくは5秒～5分間照射することにより行われる。

##### 【0037】(3) 現像工程

この露光された潜像画像を有する感光性樹脂層に、水、アルカリ水溶液、又は、酸水溶液をスプレーにより吹き付けることによって、未露光の部分の感光性樹脂層中のスチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒を溶解除去することにより、該分散媒中に分散する水不溶性又は難溶性の架橋性化合物よりなる分散質を除去することにより、画像が形成されたスクリーン印刷用版が得られる。現像は、一般に1～10分間行われる。しかし、ここで得られるスクリーン印刷用版の感光性樹脂層は水に対して難溶性であり、現像作業に耐え、十分な画像再現性が得られる耐水性を有しているが、水性インキや捺染糊を使用した印刷に耐えられないため、更なる耐水性を付与するために、本願発明においては次の加熱処理工程が必須である。

##### 【0038】(4) 加熱処理工程

###### (a) 加熱処理

上記現像により得られたスクリーン印刷用版は、一般に乾燥するために40℃程度に乾燥されるのが普通であるが、本発明においては上記乾燥温度よりも高い前記架橋性化合物が架橋反応を起こす温度、具体的な加熱処理温度としては、一般に50～220℃、好ましくは100～220℃、特に好ましくは130～200℃の温度で加熱処理工程に付することが重要である。このような加熱処理の時間としては、一般に0.5～4時間、好ましくは1～2.5時間である。このような加熱処理は、加熱又は熱線を照射することにより行われる。上記加熱は、一般にオープン等の加熱炉内で、或いは、熱風を循環送風する乾燥炉等の熱風加熱炉等により行われるのが普通である。上記熱線としては、近赤外線、遠赤外線、マイクロ波等を挙げることができる。

###### 【0039】(b) 架橋

このような加熱処理工程に付することにより、スクリーン印刷用版の感光性樹脂層中の光架橋した水に難溶性の鹼

化度50モル%以上の酢酸ビニル重合体鹼化物中に分散している水不溶性又は難溶性の架橋性化合物よりなる分散質が反応することにより高分子化したり、架橋することにより分散質を水不溶性粒子とすると共に、該水不溶性粒子が光架橋した鹼化度50モル%以上の酢酸ビニル重合体鹼化物中に残存する水酸基と反応して親水性基である水酸基を減少して水不溶化又は難溶化させたり、水酸基と反応することにより光架橋した鹼化度50モル%以上の酢酸ビニル重合体鹼化物と架橋してより巨大な分子とすることにより更に一段と不溶化させることができる。

#### 【0040】[III] スクリーン印刷用版

##### (1) 構造

この様にして得られたスクリーン印刷用版は、上記感光性樹脂組成物を用いて塗布、露光、現像、加熱又は熱線処理することにより製造されたものであることから、型枠に張られたスクリーンメッシュに部分的に樹脂層を一定の厚みで形成されて画像が形成されており、この樹脂層自体は光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物中に熱により架橋された水不溶性粒子を分散させた状態のものであり、この熱により架橋された水不溶性粒子と光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物とが架橋して一体化されて、水や有機溶剤に不溶な状態や膨潤し難い状態となっており、耐水性、有機溶剤性、耐刷性に優れたスクリーン印刷用版となっている。

##### 【0041】(2) 種類

この様なスクリーン印刷用版は、フラットスクリーン印刷機やロータリースクリーン印刷機を用いてスクリーン印刷する際に用いられる、通常のフラットスクリーン印刷版やロータリースクリーンシリンダーに感光性樹脂組成物を塗布、乾燥したロータリースクリーン印刷版として使用した場合も耐水性、有機溶剤性、耐刷性に優れたものとなる。中でも、ロータリースクリーンシリンダーを用いたロータリースクリーン印刷版として使用することが特に有用である。

##### 【0042】(3) 用途

この様なスクリーン印刷用版は、上記フラットスクリーン印刷版の感光膜面上にスクリーン印刷用のインキを載置し、この感光膜面をスキージで強く擦り、スクリーン紗を被印刷体に接触させながら摺動させることによって、この感光膜面の細孔にインキを透過させて、該感光膜の裏面側の被印刷体に被着させて画像や文字等を印刷することができる。具体的には、プリント基板等の工業部品の印刷、或いは、Tシャツやハンカチーフ等の捺染や、陶磁器、ガラス、広告看板、ポスター、エンドレス捺染、壁装床材等建築内装材等への生活に密着した製品への印刷等に幅広く適用することができる。

#### 【0043】

##### 【実施例】[I] 分散媒の製造

(製造例1) 88%鹼化ポリ酢酸ビニル(重合度1700)120gをイオン交換水1000gに溶解した。この溶液にN-メチル-γ-(p-ホルミルスチリル)ピリジニウム-ジメチル硫酸塩24gを溶解し、更に85%リン酸5gを添加して45℃で30時間攪拌しながら反応した。更に陰イオン交換樹脂を充填したカラムに反応液に通し、PH6.0の薄黄色の粘調液を作成した。測定の結果、N-メチル-γ-(p-ホルミルスチリル)ピリジニウム-ジメチル硫酸塩が88%鹼化ポリ酢酸ビニルに対し1.5mol%付加していることが確認された。

【0044】(製造例2) P-ジアゾジフェニルアミン硫酸水素塩7.5gを95%硫酸15gに溶解し、更に、パラホルムアルデヒド1gを徐々に加えて10℃で3時間攪拌した後、15℃以下に保ちながら100mlのエタノールを徐々に加え、得られた沈殿を濾過した。更に、この沈殿を各100mlのエタノールで4回よく洗い、乾燥して、緑がかった黄色のジアゾ樹脂粉体を得た。

【0045】(製造例3) 88%鹼化ポリ酢酸ビニル(重合度1700)120gをイオン交換水1000gに溶解した。この溶液にN-メチル-2-(p-ホルミルスチリル)キノリウム-ジメチル硫酸塩28gを溶解し、更に85%リン酸5gを添加して45℃で30時間攪拌しながら反応した。更に陰イオン交換樹脂を充填したカラムに反応液に通し、PH6.0の薄黄色の粘調液を作成した。測定の結果、N-メチル-2-(p-ホルミルスチリル)キノリウム-ジメチル硫酸塩が88%鹼化ポリ酢酸ビニルに対し1.2mol%付加していることが確認された。

#### 【0046】[II] 感光性樹脂組成物の製造 実施例1

スチルピリジニウム基を付加したポリビニルアルコール水溶液(製造例1で合成した水溶液)100gに、ブロックイソシアネート(日本ポリウレタン工業(株)製コロネート2513)35g混合し、ホモキサマーで10分間攪拌したところ、薄い黄色の乳白色の液体(感光性樹脂組成物)が得られた。この液状の感光性樹脂組成物を用い、スクリーン印刷用版作成の常法に従いポリエステル150メッシュに15μmの厚さに塗布し、テストパターンを描画したポジフィルムを密着して、4kw超高圧水銀灯で距離1Mで露光し、スプレーガンで水をスプレーして未露光部を洗い流したところ、硬化した感光膜で形成されたテストパターン画像が得られた。次に、この画像(版)を熱風オープンに入れ、180℃、90分の加熱処理を行った。得られたスクリーン印刷用版の評価を下記の方法に従い実施した。その結果を表1に示す。

【0047】[感光液の安定性試験] 恒温槽にて感光液を25℃にし、B型粘度計を使用し、粘度測定を行っ

た。その感光液をポリエチレン製瓶に詰め、温度30℃、湿度70%の環境試験機に入れ、10日後に取り出し、B型粘度計を使用し、25℃の時の粘度を測定した。

評価：○・・・粘度変化が0～5%であった。

△・・・粘度変化が5～20%であった。

×・・・粘度変化が20%以上であった。

【0048】〔感光膜の安定性試験〕スクリーン版作成の常法に従いポリエステル150メッシュに15μmの\*

評価：○・・・解像可能な最小の線幅が同じであった。

△・・・解像可能な最小の線幅が25μm未満で増した。

×・・・解像可能な最小の線幅が25μm以上増した。

【0049】〔適正露光時間〕スクリーン版作成の常法に従いポリエステル150メッシュに15μmの厚さに塗布し、テストパターンを描画したポジフィルムを密着して、4kw超高压水銀灯で距離1mで、露光時間を変化させて露光し、スプレーガンで水をスプレーして未露光部を洗い流したところ、硬化した感光膜で形成されたテストパターン画像が得られた。この画像のパターン部分を観察し、表・裏側の乳剤の線幅がほぼ同じになっているところを適正露光時間とした。

【0050】〔抜け性試験〕適正露光時間算出に使用した版を利用し、適正露光時間でのパターンの解像可能な最小の線幅を観察し、決定した。

【0051】〔耐水膨潤試験〕スクリーン版作成の常法に従いポリエステル150メッシュに15μmの厚さに塗布し、30×30mmの升目ポジフィルムを使用し、4kw超高压水銀灯で距離1mで、上記算出の適正露光時間にて露光し、スプレーガンで水をスプレーして未露光部を洗い流したところ、硬化した感光膜で形成された

#### 試験方法

試験切片を40℃にて24時間乾燥し、重量測定

(W<sub>0</sub>)を行った。この切片を室温で24時間水に浸漬した後、重量測定(W<sub>1</sub>)を行った。また、30×30mmのスクリーンの重量測定(W<sub>2</sub>)も行った。

$$W_1 - W_0$$

$$\text{耐水膨潤率 (\%)} = \frac{W_1 - W_0}{W_0 - W_2}$$

【0052】〔インキ汚染性の有無（反応性染料による染料汚染試験）〕

#### 染料調合

CMCを炭酸ソーダ、苛性ソーダを含む混水を加え、染料Brill Redを溶解して染料汚染試験に供した。

#### 汚染試験方法

スクリーン版に染料糊剤を2g、厚さ約1mm塗布し、ペットフィルムで両面から封じ、常温で3時間放置後、水洗乾燥し、染料汚染を観察した。

\*厚さに塗布した。この版を、温度40℃、湿度70%の環境試験機に入れ、5日後に取り出し、テストパターンを描画したポジフィルムを密着して、4kw超高压水銀灯で距離1mで、露光時間を変化させて露光し、スプレーガンで水をスプレーして未露光部を洗い流したところ、硬化した感光膜で形成されたテストパターン画像が得られた。この画像のパターン部分を観察し、適正露光時間でのパターンの抜け性を観察した。

#### 評価判定

○：染料汚染が全くなし。

△：染料汚染が僅かに認められる。

×：染料汚染が認められる。

【0053】〔耐摩耗性試験〕

#### 試験装置

先端に荷重をかけられる擦り装置の摩擦部分に、白メリヤスのウエスをかぶせ、溶剤をウエスに常に浸透させ、同一周期で往復しながら版を擦る装置。

#### 条件

荷重：2kg/cm<sup>2</sup>

擦り速度：38往復/60sec

回数：40,000回

ストローク：170mm

#### 評価判定

○：擦りの痕跡が観察されない

×：擦りの痕跡が観察される。

【0054】実施例2

スチルピリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gに、ブロックイソシアネート（日本ポリウレタン工業（株）製コロネート2513）35g、酢酸ビニルエマルジョン（ヘキスト合成（株）製MA-206）240gを混合して液状の感光性樹脂組成物を作成し、実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

【0055】実施例3

40 スチルピリジニウム基を付加したポリビニルアルコール水溶液（重合度1700、鹼化度88%、固形分12%）100gに、ブロックイソシアネート（日本ポリウレタン工業製コロネート2513）35g、酢酸ビニルエマルジョン（ヘキスト合成MA-206）240g、光重合開始剤ジエチルチオキサントロン（日本化薬（株）製KAYACURE DETX）0.2gと重合促進剤としてアミン化合物（日本化薬（株）製KAYACURE-EPA）0.1gを溶解混合したアクリレートオリゴマー（新中村化学（株）製TMPTA）を50 7g乳化・混合して液状の感光性樹脂組成物を作成し、

実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

#### 【0056】実施例4

スチルピリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gにブロックイソシアネート（日本ポリウレタン工業製コロネート2513）35g、酢酸ビニルエマルジョン（ヘキスト合成（株）製MA-206）240g、10%ジアゾ水溶液5gを混合して液状の感光性樹脂組成物を作成し、実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

#### 【0057】実施例5

スチルピリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gにブロックイソシアネート（日本ポリウレタン工業製コロネート2513）35g、酢酸ビニルエマルジョン（ヘキスト合成（株）製MA-206）240g、光重合開始剤ジエチルチオキサントン（日本化薬（株）製KAYACURE DETX）0.2gと重合促進剤としてアミン化合物（日本化薬（株）製KAYACURE-EPA）0.1gを溶解混合したアクリレートオリゴマー（新中村化学（株）製TMPTA）7gを乳化・混合して液状の感光性樹脂組成物を作成した。その感光性樹脂組成物に10%ジアゾ水溶液5gを混合し、実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

#### 【0058】実施例6

スチルピリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gにブロックイソシアネート（日本ポリウレタン工業製コロネート2507）35g、酢酸ビニルエマルジョン（ヘキスト合成（株）製MA-206）240g、10%ジアゾ水溶液5gを混合して液状の感光性樹脂組成物を作成し、実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

#### 【0059】実施例7

スチルキノリウム基を付加したポリビニルアルコール水溶液（製造例3で合成した水溶液）100gに、ブロックイソシアネート（日本ポリウレタン工業製コロネート2513）35gを混合し、ホモミキサーで10分間攪拌したところ、薄い黄色の乳白色の液体（感光性樹脂組成物）が得られた。この液状の感光性樹脂組成物を用い、スクリーン印刷用版作成の常法に従いポリエステル150メッシュに15μmの厚さに塗布し、テストパターンを描画したポジフィルムを密着して、4kw超高压水銀灯で距離1Mで露光し、スプレーガンで水をスプレーして未露光部を洗い流したところ、硬化した感光膜で形成されたテストパターン画像が得られた。この画像（版）を熱風オープンに入れ、180℃、90分の加熱処理を行った。加熱処理後のスクリーン印刷用版の評価を行

い、その結果を表1に示す。

#### 【0060】実施例8

スチルピリジニウム基を付加したポリビニルアルコール水溶液（重合度1700、鹼化度88%、固形分12%）100gに、キシレン10gを含むイミノ基型プトオキシメラミン（三井サイテック製M-508）28g、酢酸ビニルエマルジョン（ヘキスト合成 MA-206）220gを混合乳化し、水酸化カルシウム飽和水溶液でpH6.0に調整し、液状の感光性樹脂組成物を作成した。この液状の感光性樹脂組成物を用い、実施例1と同じ方法でスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

#### 【0061】実施例9

##### 感光性樹脂組成物

スチルピリジニウム基を付加したポリビニルアルコール水溶液（重合度1700、鹼化度88%、固形分12%）100gに、ブロックイソシアネート（日本ポリウレタン工業（株）製コロネート2507）35g、酢酸ビニルエマルジョン（ヘキスト合成 MA-206）240g、光重合開始剤ジエチルチオキサントン（日本化薬（株）製KAYACURE DETX）0.25gと重合促進剤としてアミン化合物（日本化薬（株）製KAYACURE-EPA）0.2gを溶解混合したアクリレートオリゴマー（新中村化学（株）製TMPTA）を7g乳化・混合して液状の感光性樹脂組成物を作成した。

#### 【0062】ロータリースクリーン印刷

上記液状の感光性樹脂組成物で、次の工程によってロータリースクリーン版を作成し、印刷を行った。

##### （1）乳剤塗布

エレクトロフォーミング法で製作されたロータリースクリーンシリンダー-TSスクリーン125（高木彫刻（株）製、直径640mmφ、長さ2,000mm、125メッシュ）を中性洗剤で洗浄、水洗し、40℃の熱風乾燥機で乾燥する。乾燥したシリンダーを自動塗布機（ストーク社製AC-2000型）に取り付け、リング状バケットに上記感光性樹脂組成物を粘度500cps/25℃に調整して、350g投入した。塗布時間16分40秒/1回（上方より下方へ）で塗布した。

##### （2）乾燥

感光性樹脂組成物を塗布した上記のロータリースクリーンシリンダーを縦状態で熱風乾燥機に入れ、40℃、1時間乾燥する。

##### （3）露光

感光性樹脂組成物を塗布・乾燥したロータリースクリーンシリンダーを露光機に載せ、画像用フィルムを巻き付け、図柄のつながり部分を合わせ、セロテープ（登録商標）で固定し、露光機（ストーク社製NEW-EP-2000）で引き続き3kwメタルハライドランプ、距離300mmで、照射窓を通して、光源の移動時間6分3

0秒/1往復、ロータリースクリーンシリンダーを20秒/10回転させながら、2往復させ、露光した。

#### (4) 現 像

ロータリースクリーンシリンダーを水槽に3分間浸漬した後、直ちに回転式、内部スプレー型の現像機（高木彫刻（株）製AD-2000）で現像した後、ロータリースクリーンシリンダーを取り出して、水スプレーによって内外部を洗浄し、室内で縦置きし、10分間水を切り、熱風乾燥機で40℃/30分間乾燥する。

#### (5) 熱処理

40℃に暖められた熱風循環乾燥炉にロータリースクリーンシリンダーを入れ、180℃に昇温し、180℃で90分間熱処理を行った。

#### (6) 印 刷

印刷装置に版を取り付け、綿布を10,000m印刷した。

印刷機 : ロータリー印刷機（東伸工業（株）製R-200型）

印刷インキ : 反応性染料を含むエマルジョンペースト（7色7種）

印刷物 : 綿布

印刷速度 : 50m/min

印刷結果を表2に示す。この結果、現在市販の重クロム酸塩を用いた従来品の感光性樹脂組成物から製造したロータリースクリーン版と同等以上の印刷結果が得られ、重クロム酸塩を使用しなくても安全性が高く、環境破壊のない感光性樹脂組成物を提供することができる。

#### 【0063】インキ汚染性の有無

10,000m印刷後のロータリースクリーンシリンダーを水洗後、乾燥し、インキの汚染性を観察した。

○ : 染料汚染が無い。

× : 染料汚染が認められる。

#### 版の感光性樹脂膜の破壊

10,000m印刷後のロータリースクリーンシリンダーを水洗後、乾燥し、乳剤の破壊、エッジ部の磨耗を観察した。磨耗については、膜厚の測定により、印刷後のロータリースクリーンシリンダーの膜厚が減少しているかどうかにより判定した。

○ : 乳剤の破壊、磨耗が無い。

× : 乳剤の破壊、磨耗が認められる。

#### 印刷画像の滲み

10,000m印刷時の印刷物を観察した。

○ : 色と色の境界線がはっきりしている。

× : 色と色の境界線が滲みによりはっきりしない。

#### 置き版の再使用

10,000m印刷後のロータリースクリーンシリンダーを水洗後、乾燥し、再度5,000mの印刷を行い、インキの汚染の有無、版の乳剤破壊について観察した。評価方法は上記と同じ。

#### 【0064】実施例10

実施例3と同一方法で作成した感光性樹脂組成物を用い、実施例1と同様にスクリーン印刷を作成した。次に、このスクリーン印刷用版を遠赤外照射装置（汎用反射板付き遠赤外ヒーター500W6本、ヒーター表面温度約500℃）を平行にセットし、遠赤外ヒーター面とスクリーン印刷用版との距離を約100mmに保ちながら、自動移動できるコンベアーで移動しながら照射する。その時のスクリーン印刷用版の感光性樹脂組成物層の表面温度は180℃である。移動速度100mm/minで、3分間照射して、得られたスクリーン印刷用版を下記の方法に従い評価した。その結果は表3に示すように、熱風による熱処理と同等の効果が得られた。

#### (1) 耐水膨張試験

実施例1の耐水膨張試験に準じて実施、評価した。

#### (2) 耐摩耗性試験

実施例1の耐摩耗性試験に準じて実施、評価した。溶剤は水、ターペンを使用。

#### (3) インキの汚染性の有無

実施例1のインキの汚染性試験に準じて実施、評価した。

#### (4) 枠とスクリーンの接着力試験

版枠（材質アルミニウム）に接着剤で接着されたスクリーンの接着強度を、島津製作所（株）製のオートグラフS-500型で、180度剥離強度を測定し、又、その時の接着剤の変色を観察した。

#### 【0065】比較例1

スチルピリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gを感光液とし、実施例1と同様にスクリーン印刷版を作成し、評価した。その結果を表1に示す。

#### 【0066】比較例2

スチルピリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gに、酢酸ビニルエマルジョン（ヘキスト合成（株）製MA-206）240gを混合して感光液を作成し、実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

#### 【0067】比較例3

スチルピリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gに、光重合開始剤ジエチルチオキサントン（日本化薬（株）製KAYACURE DETX）0.2gと重合促進剤としてアミン化合物（日本化薬（株）製KAYACURE EPA）0.1gを溶解混合したアクリレートオリゴマー（新中村化学（株）製TMPTA）を7g乳化・混合して

#### 【0068】比較例4

スチルピリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gに、酢酸ビニルエマルジョン（ヘキスト合成（株）製MA-20

6) 240 g、10%ジアゾ水溶液10 gを混合して感光液を作成し、実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

【0069】比較例5

実施例9において、感光液として重クロム酸塩型の感光液を用いて実施した以外は実施例9と同様に実施した。その結果を表2に示す。

\* 【0070】比較例6

実施例 10 において、遠赤外線の処理をしなかった以外は実施例 10 と同様に実施した。その結果を表 3 に示す。

【0 0 7 1】

【表 1】

\*

一、变

分 散 媒	必須成分	実 例										比 較 例			
		1	2	3	4	5	6	7	8	1	2	3	4		
分 散 媒	実例性適合部分酸化樹脂ビニル重合体 メチルビニルシロキサン系 スチルキソリウム塩	100	100	100	100	100	100	100	100	100	100	100	100	100	
	任意成分				5	5	5							10	
分 散 媒	阻 凝 性 化 合物	36	36	36	35	35	35	35							
	プロキソリアネン化合物 コロネート 2507														
	遊離弱酸性化合物 ブチロルメラミン								28						
分 散 媒	任意成分	240	240	240	240	240	240		220	240			240	240	
	阻 凝 性 化 合物			7 0.2		7 0.2								7 0.2	
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
分 散 媒	阻 凝 性 化 合物	80	80	80	80	80	80	80	80	80	80	80	80	80	
	任意成分														
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【0072】

【表 2】



表 2

28

		実 施 例 9	比 較 例 5 従来品（重クロム酸塩タイプ）
7色印刷後のインキ汚染性（10,000m）		○	○
版の乳剤破壊		○	○
印刷物の滲み、汚染		○	○
置き版 の 再使用	インキ汚染性の有無（5,000m）	○	○
	版の乳剤破壊	○	○

【0073】

\*10\*【表3】

表 3

			実 施 例 10	比 較 例 6
遠赤外処理の有無			有	無
評 価 結 果	耐水膨潤率		5.3	39.0
	インキ汚染性		○	×
	耐摩 耗性	水	○	×
		ターペン油	○	×

【0074】

【発明の効果】このような本発明の感光性樹脂組成物は、分散質として上記官能基を有する架橋性化合物を用いたことから、分散媒成分の光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物中に残存するOH基等の親水性基と結合して親水性基を減少させることによってより一層水に不溶性にさせると共に、光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物と架橋して一体化され、更に不溶化させることができるため、※

※得られるスクリーン印刷用版の画像を形成した感光樹脂層は、極めて高い耐水性、有機溶剤性、耐刷性を示すことができる。また、分散媒成分のスチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物を露光・現像して画像を形成した後に、架橋性化合物の硬化を行うことから、正確な画像を形成することができる。更に、重クロム酸塩を使用しない、安全性に優れ、環境破壊のない感光性樹脂組成物を提供することができる。

【手続補正書】

【提出日】平成12年2月18日（2000.2.18）

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】0006

【補正方法】変更

【補正内容】

【0006】すなわち、本発明の感光性樹脂組成物は、スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に、水不溶性又は難溶性の熱により架橋する架橋性化合物からなる分散質を分散してなること、を特徴とするものである。本発明のもう一つの発明であるスクリーン印刷用版は、スクリーンメッシュに部分的に樹脂層を形成してなり、該樹脂層が、光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼

化物中に熱により架橋された水不溶性粒子が分散されたものからなり、且つ、該熱により架橋された水不溶性粒子と光架橋された鹼化度50モル%以上の酢酸ビニル重合体鹼化物とが架橋して一体化されていること、を特徴とするものである。本発明の更なるもう一つの発明であるスクリーン印刷用版の製造方法は、スチリルピリジニウム基又はスチリルキノリウム基を含有する水可溶性の鹼化度50モル%以上の酢酸ビニル重合体鹼化物からなる分散媒中に、水不溶性又は難溶性の熱により架橋する架橋性化合物からなる分散質を分散してなる感光性樹脂組成物を、スクリーンメッシュに塗布し、乾燥させた後、露光し、現像した後で、加熱又は熱線を照射すること、を特徴とするものである。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0009



【補正方法】変更

【補正内容】

【0009】酢酸ビニル重合体

上記鹼化度50モル%以上の酢酸ビニル重合体鹼化物に用いられる酢酸ビニル重合体としては、酢酸ビニルのホモ重合体及び共重合体のいずれをも含むものである。具体的には、ポリ酢酸ビニル、酢酸ビニルとこれと共重合可能な単量体（共単量体）との共重合体である。酢酸ビニルと共重合可能な単量体としては、例えば、エチレン又はエチレン性不飽和基を持つ化合物、具体的には、アクリル酸、メタクリル酸、クロトン酸、マレイン酸、フマル酸、イタコン酸等の不飽和カルボン酸類、メチルアクリレート、メチルメタクリレート、2-エチルヘキシルアクリレート、ブチルアクリレート等のアクリレート類；アクリルアミド、メタクリルアミド、N-メチロールアクリルアミド、N,N-ジメチルアクリルアミド等のアクリルアミド類；塩化ビニル、プロピレン、ブチレン、スチレン等のビニル化合物、ジメチルアミノエチルメタクリレート、ビニルイミダゾール、ビニルピリジン、ビニルサクシミド等のカチオン性モノマー類等を挙げることができる。これらの化合物は単独または併用して使用することもでき、上記重合体中の含有量は30mol%以下が好ましい。

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0034

【補正方法】変更

【補正内容】

【0034】(4) 用途

この様な本発明の感光性樹脂組成物は、各種用途に応じて、アルミニウム、ニッケル、ステンレス等の金属板や、合成樹脂板、半導体基板、石材等の任意の基材上に塗布し、乾燥して積層するか、各種スクリーンメッシュ（ポリアミド、ポリエステル、ステンレス等のメッシュ）、ロータリースクリーンシリンダー等の表裏面又は表面に塗布し、乾燥することにより形成された、例えば1~1000 $\mu$ mの乾燥厚の感光性樹脂材料に、紫外線等からなる活性光を、例えば、紫外線の場合には波長300~450nm範囲の照射エネルギー量が10mJ/cm<sup>2</sup>以上となるようにマスク等により所定のパターンを通して照射し照射部分を硬化させた後、非照射部分の未硬化の部分をスプレー水等により除去すれば、レリーフ画像或いは画像膜が形成される。更に、この形成されたレリーフ画像或いは画像膜を50~220℃、好ましくは120~200℃の雰囲気中で加熱処理、或いは、近赤外線、遠赤外線、マイクロ波等を照射処理することにより、更に画像膜の硬化反応が進行し、耐水・耐溶剤性に優れた画像膜となる。従って、この様な感光性樹脂組成物を使用したスクリーン印刷や凸版印刷等の各種印刷版や、各種エッチングレジスト、サンドブラストエッ

チング等のレジスト膜等の用途に利用することができる。これら用途の中でもスクリーン印刷用版として用いることが好ましい。

【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0055

【補正方法】変更

【補正内容】

【0055】実施例3

スチルビリジニウム基を付加したポリビニルアルコール水溶液（重合度1700、鹼化度88%、固形分12%）100gに、ブロックイソシアネート（日本ポリウレタン工業製コロネート2513）35g、酢酸ビニルエマルジョン（ヘキスト合成 MA-206）240g、光重合開始剤ジエチルチオキサントン（日本化薬（株）製 KAYACURE DETX）0.2gと重合促進剤としてアミン化合物（日本化薬（株）製 KAYACURE-EPA）0.1gを溶解混合したアクリレートオリゴマー（新中村化学（株）製「A-TMPT」（トリメチロールプロパントリアクリレート））を7g乳化・混合して液状の感光性樹脂組成物を作成し、実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

【手続補正5】

【補正対象書類名】明細書

【補正対象項目名】0057

【補正方法】変更

【補正内容】

【0057】実施例5

スチルビリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gにブロックイソシアネート（日本ポリウレタン工業製コロネート2513）35g、酢酸ビニルエマルジョン（ヘキスト合成（株）製MA-206）240g、光重合開始剤ジエチルチオキサントン（日本化薬（株）製 KAYACURE DETX）0.2gと重合促進剤としてアミン化合物（日本化薬（株）製 KAYACURE-EPA）0.1gを溶解混合したアクリレートオリゴマー（新中村化学（株）製「A-TMPT」（トリメチロールプロパントリアクリレート））7gを乳化・混合して液状の感光性樹脂組成物を作成した。その感光性樹脂組成物に10%ジアゾ水溶液5gを混合し、実施例1同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

【手続補正6】

【補正対象書類名】明細書

【補正対象項目名】0061

【補正方法】変更

【補正内容】

【0061】実施例9

## 感光性樹脂組成物

スチルビリジニウム基を付加したポリビニルアルコール水溶液（重合度1700、鹼化度88%、固形分12%）100gに、ブロックイソシアネート（日本ポリウレタン工業（株）製コロネート2507）35g、酢酸ビニルエマルジョン（ヘキスト合成 MA-206）240g、光重合開始剤ジエチルチオキサントン（日本化薬（株）製 KAYACURE DETX）0.25gと重合促進剤としてアミン化合物（日本化薬（株）製 KAYACURE-EPA）0.2gを溶解混合したアクリレートオリゴマー（新中村化学（株）製「A-TMPT」（トリメチロールプロパントリアクリレート））7gを乳化・混合して液状の感光性樹脂組成物を作成した。

【手続補正7】

【補正対象書類名】明細書

【補正対象項目名】0064

【補正方法】変更

【補正内容】

【0064】実施例10

実施例3と同一方法で作成した感光性樹脂組成物を用い、実施例1と同様にスクリーン印刷用版を作成した。次に、このスクリーン印刷用版を遠赤外照射装置（汎用反射板付き遠赤外ヒーター500W6本、ヒーター表面温度約500℃）を平行にセットし、遠赤外ヒーター面とスクリーン印刷用版との距離を約100mmに保ちながら、自動移動できるコンベアで移動しながら照射する。その時のスクリーン印刷用版の感光性樹脂組成物層の表面温度は180℃である。移動速度100mm/minで、3分間照射して、得られたスクリーン印刷用版を下記の方法に従い評価した。その結果は表3に示すように、熱風による熱処理と同等の効果が得られた。

（1）耐水膨張試験

実施例1の耐水膨張試験に準じて実施、評価した。

（2）耐摩耗性試験

実施例1の耐摩耗性試験に準じて実施、評価した。溶剤は水、ターペンを使用。

（3）インキの汚染性の有無

実施例1のインキの汚染性試験に準じて実施、評価し

た。

（4）枠とスクリーンの接着力試験

版枠（材質アルミニウム）に接着剤で接着されたスクリーンの接着強度を、島津製作所（株）製のオートグラフS-500型で、180度剥離強度を測定し、又、その時の接着剤の変色を観察した。

【手続補正8】

【補正対象書類名】明細書

【補正対象項目名】0067

【補正方法】変更

【補正内容】

【0067】比較例3

スチルビリジニウム基を付加したポリビニルアルコール水溶液（製造例1で合成した水溶液）100gに、光重合開始剤ジエチルチオキサントン（日本化薬（株）製 KAYACURE DETX）0.2gと重合促進剤としてアミン化合物（日本化薬（株）製 KAYACURE EPA）0.1gを溶解混合したアクリレートオリゴマー（新中村化学（株）製「A-TMPT」（トリメチロールプロパントリアクリレート））7gを乳化・混合して感光液を作成した。実施例1と同様にスクリーン印刷用版を作成し、評価した。その結果を表1に示す。

【手続補正9】

【補正対象書類名】明細書

【補正対象項目名】0069

【補正方法】変更

【補正内容】

【0069】比較例5

従来品の市販されている重クロム酸乳剤を使用して、実施例9と同様にロータリースクリーン版を作成し印刷を行った。印刷結果を表2に示す。

【手続補正10】

【補正対象書類名】明細書

【補正対象項目名】0071

【補正方法】変更

【補正内容】

【0071】

【表1】

		実						施							出				範		例																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																											
分	散	集	必須成分	任意成分	架橋性化合物	任意成分	安定性	感光度 感光速度 感光保存性	露光時間 (秒)	抜け性 PM160S(白、15μm)	耐水膨潤率 (%)	インキ汚染性の有無	耐摩耗性	水 ターペン油	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498

## フロントページの続き

(51)Int.Cl. <sup>7</sup>	識別記号	F I	テーム(参考)
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		7/12	
	5 0 1	7/40	5 0 1

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 4J002 AC07Y AC08Y BB06Y BB14W  
 BB17W BC03Y BC04W BC05Y  
 BD03Y BD05W BD12Y BE02W  
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 BJ00W CD17U CK00Y CM05Z  
 CP00Y ED026 EE016 EE056  
 EH077 EN096 EP016 ER006  
 EU186 EV126 EV306 EZ006  
 FA08X FD146 FD207 HA07  
 4J011 PA40 PA63 PA68 PA83 RA02  
 RA10 SA21 SA34 SA46 SA61  
 SA63 SA64  
 4J034 BA01 BA03 DA01 DB03 DQ20  
 FA01 FB01 FB04 FC02 GA15  
 GA33 GA36 HA01 HA06 HA07  
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 HC13 HC22 HC25 HC34 HC35  
 HC44 HC46 HC52 HC61 HC63  
 HC64 HC65 HC66 HC67 HC71  
 HC73 HD01 HD04 HD12 JA41  
 JA42 MA22 MA24 QC06 RA07

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CLAIMS

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[Claim(s)]

[Claim 1] The photopolymer constituent characterized by coming to distribute the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat into the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol %.

[Claim 2] The photopolymer constituent according to claim 1 with which the hydrophobic polymer particle is distributed as a dispersoid.

[Claim 3] The photopolymer constituent according to claim 1 or 2 with which what dissolved or mixed the photopolymerization initiator to the compound which has the ethylene nature partial saturation radical which can be photopolymerized is distributed as a dispersoid.

[Claim 4] The photopolymer constituent according to claim 1 to 3 which diazo resin contains in the aqueous dispersion medium.

[Claim 5] The photopolymer constituent according to claim 1 to 4 whose cross-linking compound which constructs a bridge with heat is a block isocyanate compound.

[Claim 6] It comes to form a resin layer in a screen mesh selectively. This resin layer It consists of that by which the water-insoluble nature particle over which the bridge was constructed by heat into the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out was distributed. And the version for screen-stencil characterized by for the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out with the water-insoluble nature particle over which the bridge was constructed by this heat constructing a bridge, and unifying it.

[Claim 7] A resin layer consists of that by which the water-insoluble nature particle over which the bridge was constructed by heat into the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out, and the hydrophobic polymer particle were distributed. And the version for screen-stencil according to claim 6 with which the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out with the water-insoluble nature particle over which the bridge was constructed by this heat, and the hydrophobic polymer particle is unified by constructing a bridge.

[Claim 8] The version for screen-stencil according to claim 6 or 7 whose screen mesh is a tubed rotary screen cylinder.

[Claim 9] The manufacture approach of the version for screen-stencil characterized by to irradiate heating or a heat ray after exposing after making a screen mesh apply and dry the photopolymer constituent which comes to distribute the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat into the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol % , and developing negatives .

[Claim 10] The manufacture approach of the version for screen-stencil according to claim 9 that the hydrophobic polymer particle is distributed as a dispersoid in the photopolymer constituent.

[Claim 11] The manufacture approach of the version for screen-stencil according to claim 8 or 9 which diazo resin contains in the dispersion medium of a photopolymer constituent.

[Claim 12] The manufacture approach of the version for screen-stencil according to claim 9 to 11 that the cross-linking compound which constructs a bridge with heat is a block isocyanate compound.

[Claim 13] The manufacture approach of the version for screen-stencil according to claim 9 to 12 that a screen mesh is a tubed rotary screen cylinder.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the version for screen-stencil at the version list for screen-stencil using the photopolymer constituent and it which were suitable for especially the rotary screen about the manufacture approach of the version for screen-stencil at the version list for screen-stencil using the photopolymer constituent and it which can manufacture the various versions for printing excellent in a water resisting property, organic solvent nature, and print durability.

[0002]

[Description of the Prior Art] Conventionally, many photopolymer ingredients have been proposed as a photosensitive ingredient in which water development is possible. However, since water-soluble resin equipped with the hydrophilic radical was used, the base material resin used as a photopolymer ingredient in which water development is possible did not become the photopolymer ingredient with which the hardening image equipped with sufficient water resisting property is obtained. Especially, into the photopolymer ingredient in which water development is possible, in order to make water development nature good, the water-soluble compound, the surfactant, or the compound with a hydrophilic radical in which self-emulsification is possible is used. Consequently, a hydrophilic radical was not able to remain after the photo-curing of development, and sufficient water resisting property was not able to be given. Moreover, since contamination of the image by the reaction of the hydroxyl group of a water-soluble polymer and reactive dye which constitute an image arose in the permeate lump by the image of the pigment contained in printing paste or a color arising in using for textile printing, or using reactive dye, it was difficult to solve problems -- it is hard to perform beautiful dyeing. In order to improve such a fault, dichromate has been used abundantly as a good curing agent of a hardening property or a water resisting property from the former.

[0003]

[Problem(s) to be Solved by the Invention] However, in order for sensitization liquid and the film using dichromate to have toxicity in hexavalent chromium, to use it industrially and to have to carry out fully in consideration of environmental destruction of the wastewater at the time of platemaking, recovery of a used product, etc., operation industrial as a matter of fact is difficult for the actual condition. However, in textile printing using a rotary screen, since the water resisting property and solvent resistance which were excellent much more are required from the engine performance of the equipment, the photopolymer constituent with which current consists of the saponification object, the polyvinyl acetate emulsion, and dichromate of polyvinyl acetate is used.

[0004] On the other hand, although what shows a good water resisting property and solvent resistance like the above-mentioned dichromate as for sensitization liquid and the film using diazo resin was obtained, sensitization liquid and the film which added diazo resin in sensitization liquid had large aging, and since the hardening image of the stable quality was hard to be obtained, just before applying sensitization liquid to a screen mesh, they had to add diazo resin in sensitization liquid. For example,

what mixed diazo resin and sensitization liquid will affect an image in one week. Moreover, since a dark reaction occurs, even if it does not make what was dried after applying the mixture of diazo resin and sensitization liquid expose, crosslinking reaction arises in two - three weeks, and it has influence on an image. Therefore, whenever it applies sensitization liquid to a screen mesh, in order to have to prepare the diazo resin of a fixed rate in sensitization liquid and to have to add in it, time amount had a fault, such as being inferior to starting workability, in film production. Furthermore, the photopolymer constituent which is excellent in the water resisting property improved further and in which water development is possible is called for. Moreover, also in the flat screen-stencil currently used abundantly at general printing, it is in the inclination for water color ink to be used from safety or the trend of deenvironmental destruction as ink used at the time of printing, and sensitization liquid and a film excellent in the much more water resisting property and solvent resistance came to be called for.

[0005]

[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of the above-mentioned trouble, in order for this invention person to get the version for screen-stencil excellent in a water resisting property, organic solvent nature, and print durability After making the dispersion medium which consists of a water-soluble saponification degree % [ % of 50-99 mols ] partial saponification vinyl acetate polymer which contains the optical cross-linking radical which has optical cross-linking by itself from safety or the trend of deenvironmental destruction expose and develop By making the water-insoluble nature or the poorly soluble cross-linking compound contained as a dispersoid construct a bridge with heat By decreasing the hydrophilic radical which remains in the water which carried out optical bridge formation in a poorly soluble saponification degree % [ % of 50-99 mols ] partial saponification vinyl acetate polymer, and insolubilizing a dispersion medium in water further Based on knowledge that the version for screen-stencil excellent in a water resisting property, organic solvent nature, and print durability is obtained, it comes to complete this invention.

[0006] That is, the photopolymer constituent of this invention is characterized by coming to distribute the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat into the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol %. The version for screen-stencil which is another invention of this invention It comes to form a resin layer in a screen mesh selectively. This resin layer It consists of that by which the water-insoluble nature particle over which the bridge was constructed by heat into the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out was distributed. And it is characterized by for the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out with the water-insoluble nature particle over which the bridge was constructed by this heat constructing a bridge, and unifying it. The manufacture approach of the version for screen-stencil which is another further invention of this invention In the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol % After exposing after making a screen mesh apply and dry the photopolymer constituent which comes to distribute the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat, and developing negatives, it is characterized by irradiating heating or a radiation.

[0007]

[Embodiment of the Invention] [I] Photopolymer constituent (1) Constituent (A) In the photopolymer constituent of dispersion-medium this invention, are used as a dispersion-medium component. As a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol % A styryl pyridinium radical (\*\* 1) or a styryl kino RIUMU radical (\*\* 2) is made to add to the water-soluble vinyl acetate polymer saponification object beyond saponification degree 50 mol % as a side chain.

[0008] (a) It is the vinyl acetate polymer saponification object beyond saponification degree 50 mol % obtained by generally saponifying a vinyl acetate polymer at a rate beyond 50 mol % as a vinyl acetate



polymer saponification object beyond account saponification degree of vinyl acetate polymer saponification lifter 50 mol %, and polyvinyl alcohol is obtained by making a saponification degree into 100-mol %. In the vinyl acetate polymer saponification object beyond saponification degree 50 mol % of this invention, saponification degree % of the polyvinyl alcohol of 100 mols is also included.

[0009] As a vinyl acetate polymer used for the vinyl acetate polymer saponification object beyond vinyl acetate polymer above-mentioned saponification degree 50 mol %, both the gay polymer of vinyl acetate and a copolymer are included. Specifically, it is the copolymer of polyvinyl acetate, vinyl acetate, this, and a copolymerizable monomer (comonomer). As vinyl acetate and a copolymerizable monomer, on a compound and a concrete target with ethylene or an ethylene nature partial saturation radical, for example Unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, a crotonic acid, a maleic acid, a fumaric acid, and an itaconic acid Methyl acrylate, methyl methacrylate, 2-ethylhexyl AKURIRE - TO, Acrylate, such as butyl acrylate; Acrylamide, methacrylamide, Acrylamides, such as N-methylol acrylamide, N, and N-dimethyl acrylamide; A vinyl chloride, Vinyl compounds, such as a propylene, a butylene, and styrene; cationic monomers, such as dimethylaminoethyl meta-chestnut-TO, vinyl imidazo-RU, vinylpyridine, and vinyl SAKUSHIMIDO, can be mentioned. these compounds are independent -- or it can also be used together and used and, as for the content in the above-mentioned polymer, less than [ 30mol% ] is desirable.

[0010] as a vinyl acetate polymer saponification object beyond saponification degree above-mentioned saponification degree 50 mol %, the partial saponification of the vinyl acetate polymer is carried out -- making -- more than saponification degree 50 mol % -- it can consider as the 50-100-mol % and vinyl acetate polymer saponification object of the water solubility especially made into 70-99-mol % preferably preferably. And "more than saponification degree 50 mol %" means that the content of a vinyl alcohol part is a partial saponification vinyl acetate polymer saponification object beyond 50 mol %, when this vinyl acetate polymer is a gay polymer of vinyl acetate.

[0011] Water development is possible for the degree-of-polymerization above-mentioned vinyl acetate polymer saponification object beyond saponification degree 50 mol %, and it is for giving the constituent which can obtain the hardening film excellent in solvent resistance and a water resisting property after photo-curing. Moreover, as for the polymerization degree of the polymer, generally, it is preferably desirable the thing of 300-5,000 and to use the thing of 500-3,500 at the same reason.

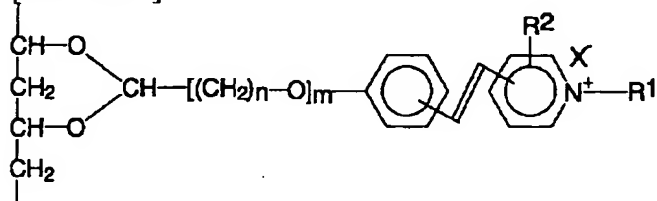
[0012] The water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical or styryl kino RIUMU radical used as a dispersion-medium component in the photopolymer constituent of this invention beyond saponification degree 50 mol % is water solubility. And it has an emulsification property or a protective colloid property for the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat, and the dispersoid which consists of a hydrophobic polymer particle used as occasion demands, and the property which is not dissolved in a common organic solvent under the usual conditions is required. Therefore, the saponification object (more than saponification degree 50 mol %) of a copolymerization object with a compound with the saponification object (more than saponification degree 50 mol %) of a vinyl acetate polymer, vinyl acetate and ethylene, or an ethylene nature partial saturation radical, polyvinyl alcohol polymers, or these derivatives are suitable. moreover -- as the derivative of a polymer saponification object -- formaldehyde, an acetaldehyde, a butyraldehyde, and benzaldehyde etc. -- the added object can be used. As for the amount of addition, less than [ 30mol% ] is desirable. Specifically, these side-chain derivatives can be mentioned, including the acetal ghost by low-grade (C1-C4) acetal ghost [ , such as formal-izing of saponification polyvinyl acetate, or butyral-izing, ] and p-benzaldehyde sulfonic-acid, beta-butyraldehyde sulfonic-acid, o-benzaldehyde sulfonic-acid, 2, and 4-benzaldehyde disulfon acid etc.

[0013] (b) Set to the photopolymer constituent of optical cross-linking basic invention, and it is a water-soluble vinyl acetate polymer saponification object beyond saponification degree 50 mol %. As the styryl pyridinium radical (\*\* 1) contained as a side chain in inside, or a styryl kino RIUMU radical (\*\* 2), it is the optical cross-linking radical which has optical cross-linking by itself. The water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical or styryl kino RIUMU

radical used in this invention beyond saponification degree 50 mol % makes the styryl pyridinium radical (\*\* 1) or styryl kino RIUMU radical (\*\* 2) expressed with the following general formula (I) and (II) add. General formula (I)

[0014]

[Formula 1]

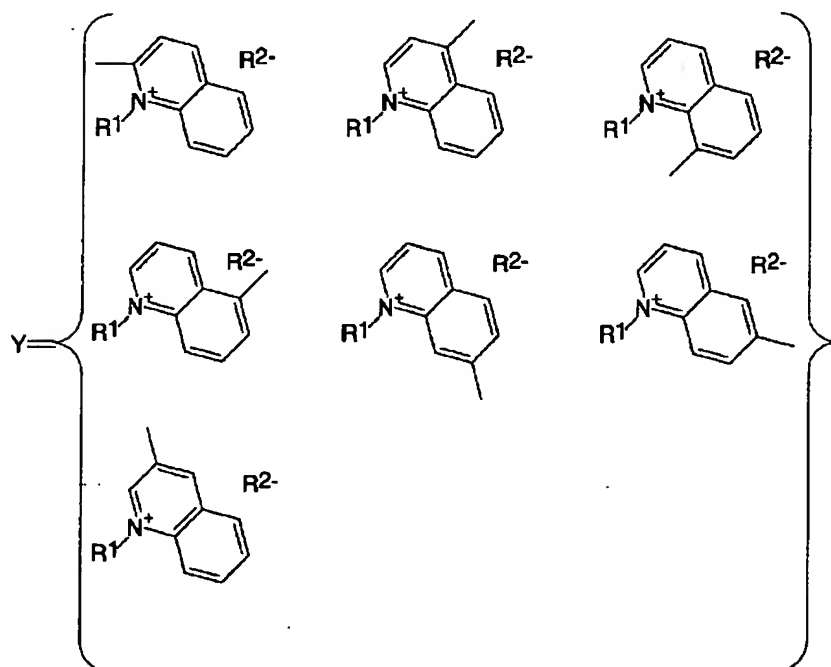
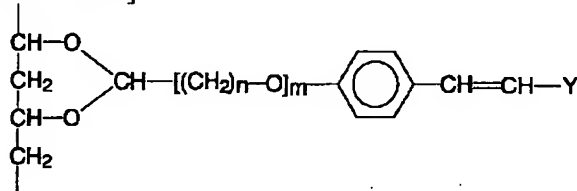


[0015] (\*\* 1)

General formula (II)

[0016]

[Formula 2]



[0017] (\*\* 2)

However, R<sup>1</sup> shows a hydrogen atom, an alkyl group, or an aralkyl radical among the above-mentioned general formula (I) and (II), these may also include hydroxyl, a carbamoyl group, ether linkage, and an unsaturated bond, and R<sup>2</sup> shows a hydrogen atom or a low-grade alkyl group. X - The mixture of halogen ion, phosphoric-acid ion, p-toluenesulfonic-acid ion, or these anions is shown, and, as for 0 or

1, and n, m shows the integer of 1-6. The partial saponification vinyl acetate polymer which has the above still BAZORIUM radicals, and its manufacturing method are already known (JP,55-23163,A, JP,55-62905,A, and JP,55-62405,A each official report). the amount of addition of the styryl pyridinium radical of photodimerization nature, and a styryl quinolinium radical -- general -- 0.2-7.0-mol % -- it is 0.5-5.0-mol % preferably. There is an inclination whose image formation is fully impossible in it being under the above-mentioned range. Moreover, when the above-mentioned range is exceeded, there is an inclination for dissolved water in fuel to worsen. As for the dispersion-medium component which consists of a water-soluble vinyl acetate polymer saponification object containing these styryls pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol %, diluting bywater is common.

[0018] (B) Water-insoluble nature or a poorly soluble cross-linking compound (dispersoid)

(a) As a dispersoid which consists of the water-insoluble nature or the poorly soluble cross-linking compound used as a dispersoid component in the photopolymer constituent of cross-linking compound this invention, it is the cross-linking compound which constructs a bridge with heat. They are the compound which has a radical with active hydrogen, such as water-soluble-OH radical of the vinyl acetate polymer beyond saponification degree 50 mol % used as a dispersion-medium component by irradiating heating or a heat ray as a cross-linking compound which constructs a bridge with heat, or a polyvinyl alcohol polymer, -COOH radical and -NH<sub>2</sub>, and -SH, and the functional group which can react, and the compound which has two or more functional groups preferably. Such a functional group As an example, an aldehyde group, an isocyanate radical, an alkoxy group, a glycidyl group, an ethylene nature partial saturation radical, the amino group, and diester can be mentioned, for example.

Specifically as a compound which has such a functional group, ethylene nature partial saturation radical content compounds, such as metal chelate compound, such as dialdehyde compounds, such as alkoxy compounds, such as amino compounds, such as thiourea, a melamine, and benzoGUAMIN, a methylol-ized melamine, a BUCHIRORU-ized melamine, and methylol acrylamide, glyoxal, and a glutaraldehyde, a block isocyanate compound shown in the following, cobalt, titanium, a zirconium, and molybdenum, an acryloyl radical, a meta-acryloyl radical, S Kurile amide group, and a vinyl ether radical etc. can be mentioned Furthermore, it can be more effectively used by making these compounds live together. The photopolymer constituent which used especially the block isocyanate compound also in the compound which has these functional groups is desirable from excelling in long term stability.

[0019] The block isocyanate compound above-mentioned block isocyanate compound carries out the mask of the isocyanate radical of an isocyanate compound by the block agent (for example, compounds, such as a caprolactam which has active hydrogen, activity methylene, and an oxime), in ordinary temperature, although it is stable, if it heats (usually 120 degrees C or more), a block agent will dissociate and an activity isocyanate radical will be reproduced. As an isocyanate compound used for the above-mentioned block isocyanate compound It is what two or more isocyanate radicals have. As an example of such a compound 2, 6-tolylene diisocyanate (2, 6-tolylene diisocyanate), 2, 4 tolylene diisocyanate (2, 4-tolylene diisocyanate), 4 and 4-diphenyl methane diisocyanate, 1,5-naphthalene diisocyanate, Aromatic series diisocyanate, such as m-xylenediisocyanate and m-tetramethyl xylenediisocyanate, Methyl hexamethylene di-isocyanate, 2 and 2, 4 trimethyl hexamethylene di-isocyanate, Aliphatic series isocyanates, such as 2, 4, and 4 trimethyl hexamethylene di-isocyanate, Isophorone diisocyanate, hydrogenation 4, 4' diphenyl methane diisocyanate, Alicycle group diisocyanate, such as hydrogenation m-xylenediisocyanate, Triphenylmethane triisocyanate, polymethylene polyphenyl isocyanate, Polyfunctional aromatic series isocyanate compounds, such as the trimethylol propane adduct object and isocyanurate object of tolylene diisocyanate, polymeric methane diisocyanate, and other prepolymer isocyanates, etc. can be mentioned. the block isocyanate compound which carried out the mask to these isocyanate compounds by the block agent is independent -- or it can use together and use. As for the above-mentioned block isocyanate compound, it is desirable that it is the emulsification block isocyanate compound which carried out emulsification distribution into the dispersion-medium component which consists of a water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical in a photopolymer constituent or a styryl

kino RIUMU radical beyond saponification degree 50 mol % and which was distributed minutely. Consequently, the stable photopolymer constituent is obtained. Moreover, it may mix with other compounds, the compound which is not emulsified if independent may also be made to emulsify, and you may use it further, dissolving in an organic solvent (hydrophobicity is desirable). It is not necessary to be the compound which the polymer and prepolymer which are compatible in the block isocyanate compound emulsified and distributed could be mixed and used into the dispersion-medium component, and such a polymer and a prepolymer not necessarily had -OH radical, -COOH radical and two -NH(s), -sulfhydryl group, etc., and was rich in an isocyanate radical and reactivity. However, what has good emulsification / distribution property is desirable in water at poor solubility.

[0020] (b) The cross-linking compound which constructs a bridge with the water-insoluble nature or the poorly soluble heat used as a dispersoid component in the water-insoluble nature of a dispersoid component, or the photopolymer constituent of poorly soluble this invention From it having to distribute in the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical or styryl kino RIUMU radical contained in the photopolymer constituent of this invention beyond saponification degree 50 mol % It is important that they are water-insoluble nature or a poorly soluble thing. Moreover, the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat First, photocuring of the dispersion-medium component in a photopolymer constituent is carried out by making a photopolymer constituent expose through a mask film at an exposure process. Furthermore, after carrying out dissolution clearance of the unexposed dispersion-medium component and making an image form by carrying out water development, in order to stiffen a dispersoid component by irradiating heating or a heat ray at heating or a heat radiation process at a dispersoid component It is important that a dispersoid component dissolves by water and is not extracted in the development process at the time of the image formation which is a before process.

[0021] rack a pons -- by using the cross-linking compound which has the above-mentioned functional group as such a dispersoid While making it water further at insolubility by combining with hydrophilic radicals, such as an OH radical which remains in the vinyl acetate polymer saponification object beyond saponification degree 50 mol % with which optical bridge formation of the dispersion-medium component was carried out, and decreasing a hydrophilic radical Since a bridge is constructed with the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out, and it is unified and can be made to insolubilize further, the sensitization resin layer in which the image of the version for screen-stencil obtained was formed can raise a water resisting property, organic solvent nature, and print durability further.

[0022] (C) The dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical or styryl kino RIUMU radical contained in the photopolymer constituent of blending-ratio-of-coal this invention beyond saponification degree 50 mol %, The blending ratio of coal with the dispersoid which consists of a cross-linking compound which constructs a bridge with the water-insoluble nature or the poorly soluble heat distributed in this dispersion medium the solid content 100 weight section in an aqueous dispersion medium -- receiving -- a cross-linking compound -- general -- the 10 - 500 weight section -- desirable -- the 30 - 400 weight section -- it is especially blended at a rate of the 50 - 300 weight section preferably. The inclination which is not enough is in an improvement of a deck watertight luminaire and solvent resistance under in the above-mentioned range. Moreover, when the above-mentioned range is exceeded, there is an inclination emulsion stability becomes [ an inclination ] easy to carry out a separation deposit bad. Furthermore, it coats, and the sensitization resin film after desiccation has a strong tuck, and has the inclination for the bleeding of a cross-linking compound to become intense.

[0023] (2) Although the photopolymer constituent of constituent this invention of arbitration consists of the above-mentioned constituent fundamentally, it is desirable to blend the compound which has an ethylene nature partial saturation radical containing the hydrophobic polymer particle shown below as a component of arbitration, a photoinitiator cross linking reagent, and a photopolymerization initiator.

[0024] (A) A water resisting property can be further raised by making the dispersoid which consists of a

hydrophobic polymer particle into the hydrophobic polymer particle above-mentioned photopolymer constituent contain. The dispersion liquid of the giant-molecule polymer which the water-insoluble nature giant-molecule distribution object had the emulsion obtained by the inside of a polymerization process distributed by remaining as it is, and was distributed [ polymer / giant-molecule ] by the main dispersion medium in water and water are used. It is easily mixable in the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol %, and the dispersion liquid of the giant-molecule polymer containing such a hydrophobic polymer particle can be used if neither condensation nor precipitate is caused. As for especially the photopolymer constituent with which such a hydrophobic polymer particle was distributed, it is desirable that 50 micrometers or less of mean particle diameter of a hydrophobic polymer particle are 15 micrometers or less. It is desirable to the solid content 100 weight section in a photopolymer constituent 5 - 95 weight section and to make the loadings of such a hydrophobic polymer particle component into 20 - 85 weight section preferably as solid content. When there is an inclination for the waterproof improvement effectiveness to the hardening film to be unable to show up [ the loadings of a hydrophobic polymer particle component ] easily under in the above-mentioned range and the above-mentioned range is exceeded, there is an inclination for an image with sufficient repeatability with bad development nature to be hard to be obtained. The dispersion liquid of the macromolecule polymer which such a hydrophobic polymer particle component had the emulsion obtained by the inside of a polymerization process distributed by remaining as it is, and was distributed [ polymer / macromolecule ] by the main dispersion medium in water and water are used. The high molecular compound and naturally-occurring-polymers compound which were compounded are sufficient as these hydrophobic polymer particle components. printing the effectiveness of the hydrophobic polymer particle component of this invention improves the water resisting property of the formed image, and using improvement in definition, and water color ink and the aquosity paste of a photo-curing image as the result -- improvement relation in print durability is carried out.

[0025] As the above-mentioned hydrophobic polymer particle, they are polyvinyl acetate, vinyl acetate / ethylene copolymer, and vinyl acetate / acrylic ester copolymer (as acrylic ester here), for example. for example, there are a methyl acrylate, 2-ethylhexyl acrylate, etc. An acrylic-acid (meta) polymer, styrene / butadiene copolymer, a methyl methacrylate / butadiene copolymer, Acrylonitrile / butadiene copolymer, a chloroprene polymer, an isoprene polymer, a polyvinyl chloride, a polyvinylidene chloride, polystyrene, silicone resin, polyethylene, polyurethane, a fluororesin, etc. can be mentioned. These hydrophobic polymer particle can mention the polyvinyl acetate emulsion obtained more in process, ethylene and a vinyl acetate copolymer emulsion, a vinyl acetate acrylic copolymer emulsion, ethylene and the polymerization vinyl acetate acrylic copolymerization emulsion of 3 yuan, a vinyl chloride and a vinyl acetate emulsion, an acrylic emulsion, a styrene butadiene latex emulsion, an MBR latex emulsion, an acrylonitrile-butadiene rubber latex emulsion, a chloroprene rubber-latex emulsion, a vinylidene-chloride emulsion, etc. As synthetic macromolecule dispersion, polyethylene dispersion, polyolefine ionomer dispersion, urethane ionomer dispersion, etc. are useful. Moreover, what distributed synthetic macromolecule pulverized coal and purification starch can be used.

[0026] (B) Although the photopolymer constituent of photoinitiator cross linking reagent this invention can obtain enough hardening images by the optical cross-linking radical which has optical cross-linking contained in an aquosity dispersion-medium component, it can obtain the hardening image which was further excellent by adding a photoinitiator cross linking reagent (diaz resin) further. However, in adding only a photoinitiator cross linking reagent, the preservation stability of a photopolymer constituent gets worse, or there is also a fault to which photosensitivity falls. As such a diazo resin compound, a dimethoxy diphenyl ether condensate, the paraformaldehyde condensate of a 4-diazo 3-methoxy diphenylamine, or paraformaldehyde condensate [ of a p-diazo diphenyl amine ] or 4, and 4 '4, 4' dimethoxy diphenyl ether condensate can be mentioned. Furthermore, a new diazo compound given in JP,5-125031,A etc. is useful. When making diazo resin contain, it is desirable to the solid content 100 weight section in a photopolymer constituent 0.1 - 4 weight section and to contain at a rate of the 0.2 -

2.5 weight section preferably as solid content.

[0027] (C) If a photopolymerization initiator is used for a compound with the compound ethylene nature partial saturation radical which has an ethylene nature partial saturation radical containing a photopolymerization initiator, dissolving or mixing, the polymerization of this mixture will be carried out by light, and it will be macromolecule-ized. Moreover, an aqueous dispersion-medium component and a dispersoid, and graft polymerization bridge formation are also started simultaneously, and the deck watertight luminaire and the solvent resistance of a hardened material are raised. a compound with an ethylene nature partial saturation radical -- carrying out -- it is insoluble in water and what can be easily emulsified in a component (A) solution is desirable.

[0028] the compound which has an ethylene nature partial saturation radical -- it is the compound with which it has one or more ethylene nature partial saturation radicals, such as an acryloyl radical, a meta-acryloyl radical, an allyl group, a vinyl ether radical, an acrylamide radical, and a meta-acrylamide radical, and an insoluble or poorly soluble thing has an acryloyl radical and one or more meta-acryloyl radicals preferably desirable especially in water as a compound which has such an ethylene nature partial saturation radical. As such a compound, specifically For example, pen TAERISURITORUTORI (meta) acrylate, Pentaerythritol tetrapod (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, Trimethylolethane tri(metha)acrylate, dipentaerythritol hexa (meta) acrylate, Ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Tetra-ethylene GURIKORUJI (meta) acrylate, hexa ethylene GURIKORUJI (meta) acrylate, a jib -- ROMUHEO pentyl GURIKORUJI (meta) acrylate, 2, and 8 jib -- hawk alcoholic multiple-valued acrylate, such as ROM neopentyl GURIKORUJI (meta) acrylate, -- 2 and 2-bis(4-meta-KURIROKISHI ethoxy phenyl) propane, 2, and 2-(4-acryloxy ethoxy phenyl) propane, Epoxy acrylate, such as an acrylic acid of the epoxy resin of bisphenol A and an epichlorohydrin system, or a methacrylic-acid addition product, An addition product with the acrylic acid of trimethylolpropane triglycidyl ether or methacrylic acid, the urethane (meta) acrylic compound obtained at the reaction of TORIHEKISA methylene G SOSHINETO and the acrylic (meta) mono-acid ester of dihydric alcohol are mentioned. These compounds can use together and use independent or two sorts or more. As for the photopolymer constituent with which the compound which has an ethylene nature partial saturation radical containing such a photopolymerization initiator was distributed, it is desirable that 20 micrometers or less of mean particle diameter of the compound which has an ethylene nature partial saturation radical are especially 10 micrometers or less. It is desirable to the solid content 100 weight section in a photopolymer constituent 0.5 - 70 weight section and to make preferably into 1 - 50 weight section the loadings of the compound component which has such an ethylene nature partial saturation radical. When there is an inclination for the waterproof improvement effectiveness at the time of development to be unable to show up [ the loadings of the compound component which has an ethylene nature partial saturation radical ] easily under in the above-mentioned range and the above-mentioned range is exceeded, there is an inclination for an image with sufficient repeatability with bad development nature to be hard to be obtained.

[0029] In order to make the photopolymerization initiator above-mentioned polymerization nature compound react promptly by optical exposure, it is common to add a photopolymerization initiator. As for such a photopolymerization initiator, it is desirable that dissolve or dissolve in the above-mentioned polymerization nature compound, and homogeneity is mixed. As such a photopolymerization nature initiator, thioxan ton derivatives, such as anthraquinone, such as a benzophenone, benzoin alkyl ether, a MIHIRAZU ketone, benzyl, the benzyl dialkyl ether, and TASHARU butyl anthraquinone, a chloro thioxan ton, and an isopropyl thioxan ton, etc. are mentioned. Furthermore, photopolymerization accelerators, such as p-dimethylamino isoamyl benzoate ester and p-dimethylamino ethyl benzoate ester, may be mixed. These are effective when speeding up the polymerization cure rate at the time of using a benzophenone system and a thioxan ton system. Generally the above-mentioned photopolymerization nature initiator is blended at a rate of 1 - 10 weight section to the compound 100 weight section which has an ethylene nature partial saturation radical.

[0030] (D) Although it is desirable that the above-mentioned arbitration component is blended as for the photopolymer constituent of other arbitration component this inventions, it can add further the additive



component usually contained in this kind of photopolymer constituent to arbitration. As an additive component of such arbitration, the solid content 100 weight section in the above-mentioned photopolymer constituent is received, for example. The emulsion stabilizer below the 0.5 weight section As a solubilizing agent of the compound containing the cross-linking compound and the ethylene nature partial saturation radical which can be photopolymerized which constructs a bridge with heat The coloring agent which makes images, such as a color and a pigment, legible for an organic solvent without the water and the miscibility below 30 weight sections further, a defoaming agent, etc. can be added within limits usually added to these 100 weight sections. Moreover, inorganic fine particles can be added by within the limits below 30 weight sections to the solid content 100 weight section in a photopolymer constituent as an extending agent or a tack inhibitor.

[0031] (3) In order to obtain the photopolymer constituent of this invention from the preparation above-mentioned constituent and arbitration component of a photopolymer constituent, it can usually prepare by the approach shown below.

The manufacture partial saponification vinyl acetate polymer of a photosensitive polymer is dissolved in water, the compound containing a styryl pyridinium radical or a styryl kino RIUMU radical is dissolved in this solution, it adds and a phosphoric acid is made to react further. The photosensitive polymer water solution which consists of a partial saponification polyvinyl acetate polymer with which the styryl pyridinium radical or styryl kino RIUMU radical which becomes the column filled up with anion \*\*\*\*\* from the viscous liquid of through and thin yellow added this reaction mixture is obtained.

[0032] Milk The photopolymer constituent of this invention is obtained by adding the cross-linking compound which constructs a bridge with heat, or the cross-linking compound which constructs a bridge with the heat which mixed the little organic solvent used if needed in the photosensitive polymer water solution of-izing \*\*, and stirring and emulsifying with a kneader, a homomixer screw-type agitator, etc. in it.

[0033] The photopolymer constituent of this invention improved further is obtained by adding and emulsifying combination of an arbitration component, and also the photopolymerization nature compound which carried out dissolution mixing of a photopolymerization initiator or the photopolymerization accelerator if needed, and adding the diazo compound which is a photoinitiator cross linking reagent, and mixing [ \*\*\*\* / mixing hydrophobic giant-molecule polymer dispersion liquid, and a coloring agent and a defoaming agent ] if needed. In addition, it is not fixed to the above-mentioned sequence and the addition sequence of each component can change addition sequence in the range which the problem at the time of mixing of condensation, separation, a deposit, etc. does not produce. However, since the stability of a diazo compound in the inside of a water solution is not good, the preservation stability of sensitization liquid tends to fall. Therefore, adding just before an activity is desirable.

[0034] (4) business a way -- such a photopolymer constituent of this invention It responds to various applications. Metal plates, such as aluminum, nickel, and stainless steel, [ whether it applies on the base material of arbitration, such as a synthetic-resin plate, a semi-conductor substrate, and a stone and a laminating is dried and carried out, and ] Various screen mesh (mesh, such as a polyamide, polyester, and stainless steel), Applied to a table rear face or front faces, such as a rotary screen cylinder, and were formed by drying. For example, the activity light which becomes a photopolymer ingredient with a dry thickness of 1-1000 micrometers from ultraviolet rays etc. For example, after in the case of ultraviolet rays having irradiated through the predetermined pattern with the mask etc. so that the amount of exposure energy of the wavelength the range of 300-450nm might become two or more 10 mj/cm, and stiffening an exposure part, If spray water etc. removes the part which is not hardened [ of a non-irradiating part ], a relief image or the image film will be formed. Furthermore, about this formed relief image or image film, by carrying out exposure processing of heat-treatment or a near infrared ray, far infrared rays, the microwave, etc. in a 120-200-degree C ambient atmosphere preferably, the hardening reaction of the image film advances further and 50-220 degrees C becomes the image film excellent in a deck watertight luminaire and solvent resistance. Therefore, it can use for the application of resist film, such as the various printing versions which used such a photopolymer constituent, such as screen-stencil

and Toppan Printing, and various etching resist, sandblasting etching, etc. It is desirable to use as a version for screen-stencil also in these applications.

[0035] [II] The manufacture approach of the version for screen-stencil as a desirable application of the photopolymer constituent which is the manufacture above of the version for screen-stencil, and was made and obtained is indicated in a detail below.

It responds to spreading / desiccation process application. (1) Aluminum, stainless steel, the flat screen-stencil frame which manufactured metal cylindrical raw materials, such as steel, in the square or the rectangle -- various screen mesh -- sha -- with the bucket for the flat screen versions for the flat screen version which carried out the flare or [ carrying out the laminating of the above-mentioned photopolymer constituent by predetermined thickness by repeating spreading and a desiccation process according to a conventional method ] -- or On the metal rotary screen cylinder formed by the electroforming method, with a ring-like bucket According to a conventional method, the photopolymer film with which 0.5-1,000 micrometers of 1-400 micrometers of desiccation thickness generally consist of a photopolymer constituent with a thickness of 1-200 micrometers preferably especially is formed 1 time or by repeating several times in spreading and the desiccation process of the above-mentioned photopolymer constituent. Thus, an overcoat layer can also be formed in front flesh-side both sides of the photopolymer film which consists of an obtained photopolymer constituent for this film protection. The PS plate for screen-stencil can be obtained by this. It is polyethylene about the approach and sensitization liquid which face obtaining the version for screen-stencil and apply sensitization liquid directly, Scree which applies and dries, obtains the 5-1,000-micrometer film, and applied water or sensitization liquid for this film on plastic films, such as a polyvinyl chloride and polyester There is the approach (approach called the method between [ so-called ] direct) of imprinting on - N. The photopolymer constituent of this invention can form a film by such approach.

[0036] The film which consists of a negative film or a positive film the film which becomes the screen stretched by the exposure process above-mentioned shuttering from a photopolymer constituent is minded. (2) Ultraviolet rays, By irradiating beams of light, such as a visible ray and an argon laser, and exposing them The dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical in the photopolymer layer by the side of the rear face of the part which the image is drawn on this film and does not penetrate light, or a styryl kino RIUMU radical beyond saponification degree 50 mol % serves as unexposed, and does not harden. It can harden by exposing the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object beyond saponification degree 50 mol % which, on the other hand, contains the styryl pyridinium radical in the photopolymer layer by the side of the rear face of a part where the image is not drawn on this film, or a styryl kino RIUMU radical, and carrying out lifting light bridge formation of the photoreaction, and a latent-image image can be made to form in the photopolymer layer of this part. The output of 1-15kW, exposure can use the light source of a 2-6kW ultrahigh pressure mercury lamp, a high-pressure mercury-vapor lamp, a metal halide content high-pressure mercury-vapor lamp, etc. preferably, and, generally is preferably performed by irradiating for [ 5 seconds - ] 5 minutes preferably for [ 3 seconds - ] 20 minutes from distance (0.2-1.5m) 0.1-2m.

[0037] In the photopolymer layer which has this exposed latent-image image, \*\*\*\*\* (3) Water, an alkali water solution, Or by carrying out dissolution clearance of the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object beyond saponification degree 50 mol % which contains the styryl pyridinium radical in the photopolymer layer of an unexposed part, or a styryl kino RIUMU radical by spraying an acid water solution with a spray By removing the dispersoid which consists of the water-insoluble nature or the poorly soluble cross-linking compound distributed in this dispersion medium, the version for screen-stencil with which the image was formed is obtained.

Generally development is performed for 1 - 10 minutes. However, although it has the water resisting property from which the photopolymer layer of the version for screen-stencil obtained here is poorly soluble, and is equal to a development activity to water, and sufficient image repeatability is acquired, since printing which used water color ink and printing paste cannot be borne, in order to give the further water resisting property, in the invention in this application, the following heating down stream



processing is indispensable.

[0038] (4) Heating down stream processing (a) Although about 40 degrees C usually dries in order to dry the version for screen-stencil obtained by the heat-treatment above-mentioned development generally Generally in this invention, 100-220 degree C of 50-220 degree C of \*\*\*\*\* especially given to heating down stream processing at the temperature of 130-200 degrees C preferably are preferably important as the temperature from which said cross-linking compound higher than the above-mentioned drying temperature starts crosslinking reaction, and concrete heat-treatment temperature. Generally as time amount of such heat-treatment, it is 1 - 2.5 hours preferably for 0.5 to 4 hours. Such heat-treatment is performed by irradiating heating or a heat ray. As for the above-mentioned heating, it is common to be performed by hot blast heating furnaces, such as a drying furnace which is generally in heating furnaces, such as oven, or carries out circulation air blasting of the hot blast, etc. As the above-mentioned heat ray, a near infrared ray, far infrared rays, microwave, etc. can be mentioned.

[0039] (b) rack a pons -- by \*\*\*\*\* given to such heating down stream processing When the dispersoid which consists of the water-insoluble nature or the poorly soluble cross-linking compound currently distributed in the vinyl acetate polymer saponification object beyond [ poorly soluble ] saponification degree 50 mol % reacts to the water which carried out optical bridge formation in the photopolymer layer of the version for screen-stencil, macromolecule-ize, or While making a dispersoid into a water-insoluble nature particle by constructing a bridge, this water-insoluble nature particle reacts with the hydroxyl group which remains in the vinyl acetate polymer saponification object beyond saponification degree 50 mol % which carried out optical bridge formation, and decrease, and insolubilize [ water-] or grit [ difficulty-] the hydroxyl group which is a hydrophilic radical, or It can be made to insolubilize further much more by reacting with a hydroxyl group by constructing a bridge with the vinyl acetate polymer saponification object beyond saponification degree 50 mol % which carried out optical bridge formation, and considering as a huger molecule.

[0040] [III] Version for screen-stencil (1) Style The version for screen-stencil obtained by \*(ing) thus carrying out Use the above-mentioned photopolymer constituent, apply and from being manufactured by exposure, development, heating or heat ray processing Form a resin layer in the screen mesh stretched by shuttering by fixed thickness selectively, and the image is formed. This resin layer itself is a thing in the condition of having distributed the water-insoluble nature particle over which the bridge was constructed by heat into the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out. It is constructed a bridge and unified, the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out with the water-insoluble nature particle over which the bridge was constructed by this heat is in an insoluble condition and the insoluble condition of being hard to swell at water or an organic solvent, and it has become the version for screen-stencil excellent in a water resisting property, organic solvent nature, and print durability.

[0041] (2) seed a kind -- such a version for screen-stencil becomes the thing excellent in a water resisting property, organic solvent nature, and print durability, also when it is used for the usual flat screen-stencil version and usual rotary screen cylinder which are used in case it screen-stencils using a flat screen printer or a rotary screen printing machine as a rotary screen printing version which applied and dried the photopolymer constituent. Especially the thing used especially as a rotary screen printing version which used the rotary screen cylinder is useful.

[0042] (3) business a way -- by making it slide, laying the ink for screen-stencil on the film side of the above-mentioned flat screen-stencil version, grinding this film side against a squeegee strongly, and contacting screen \*\* to a printing hand-ed, such a version for screen-stencil can make the pore of this film side able to penetrate ink, can be made to be able to put on the printing hand-ed by the side of the rear face of this film, and can print an image, an alphabetic character, etc. Specifically, it is broadly applicable to printing to the product stuck to the life to building inner package material, such as textile printing of printing of industrial components, such as a printed circuit board, or a T-shirt, a handkerchief, etc., pottery, glass, an advertising signboard, a poster and endless textile printing, and wall covering flooring, etc.

[0043]

[Example] [I] 120g (polymerization degree 1700) of 88% (example 1 of manufacture) saponification polyvinyl acetate of manufactures of a dispersion medium was dissolved in 1000g of ion exchange water. 24g of N-methyl-gamma-(p-formyl styryl) pyridinium-dimethyl sulfates was dissolved in this solution, and it reacted, having added 5g of phosphoric acids 85 more%, and stirring at 45 degrees C for 30 hours. Furthermore, the viscous liquid of through and the thin yellow of PH6.0 was created in the column filled up with anion exchange resin at reaction mixture. the result of measurement -- an N-methyl-gamma-(p-formyl styryl) pyridinium-dimethyl sulfate -- 88% saponification polyvinyl acetate -- receiving -- 1.5-mol% -- having added was checked.

[0044] (Example 2 of manufacture) It is \*\* to 15 degrees C or less after dissolving 7.5g of P-diazo diphenylamine hydrogensulfates in 15g of sulfuric acids 95%, adding paraformaldehyde 1g gradually further and stirring at 10 degrees C for 3 hours. The precipitate which added 100ml ethanol gradually with \*\*, and was obtained was filtered. Furthermore, it washed this precipitate each with 4 sufficient times by 100ml ethanol, and it dried and the diazo resin fine particles of the yellow which green cut were obtained.

[0045] (Example 3 of manufacture) 120g (polymerization degree 1700) of saponification polyvinyl acetate was dissolved in 1000g of ion exchange water 88%. 28g of N-methyl-2-(p-formyl styryl) kino RIUMU-dimethyl sulfates was dissolved in this solution, and it reacted, having added 5g of phosphoric acids 85 more%, and stirring at 45 degrees C for 30 hours. Furthermore, the viscous liquid of through and the thin yellow of PH6.0 was created in the column filled up with anion exchange resin at reaction mixture. the result of measurement -- an N-methyl-2-(p-formyl styryl) kino RIUMU-dimethyl sulfate -- 88% saponification polyvinyl acetate -- receiving -- 1.2-mol% -- having added was checked.

[0046] [II] 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the manufacture example 1 still pyridinium radical of a photopolymer constituent -- block isocyanate (coronate 2513 made from Japanese Polyurethane Industry) 35g -- the place which was mixed and was stirred for 10 minutes by the homomixer -- the milk of thin yellow -- the white liquid (photopolymer constituent) was obtained. Using this liquefied photopolymer constituent, according to the conventional method of the version creation for screen-stencil, it applied to 150 meshes of polyester at the thickness of 15 micrometers, the positive film which drew the test pattern was stuck, and it exposed by distance 1M with 4kw ultrahigh pressure mercury lamp, and when the spray of the water was carried out with the spray gun and the unexposed part was flushed, the test pattern image formed by the hardened film was obtained. Next, this image (version) was put into hot blast oven, and 180 degrees C and heat-treatment for 90 minutes were performed. Assessment of the obtained version for screen-stencil was carried out according to the following approach. The result is shown in a table 1.

[0047] Sensitization liquid was made into 25 degrees C with the [stability test of sensitization liquid] thermostat, the Brookfield viscometer was used, and measurement of viscosity was performed. The sensitization liquid was put in the bottle made from polyethylene, it put into the environmental-test machine of the temperature of 30 degrees C, and 70% of humidity, ejection and a Brookfield viscometer were used ten days after, and the viscosity at the time of 25 degrees C was measured.

評価：○・・・粘度変化が0～5%であった。

△・・・粘度変化が5～20%であった。

×・・・粘度変化が20%以上であった。

[0048] According to the conventional method of the [stability test of film] screen version creation, it applied to 150 meshes of polyester at the thickness of 15 micrometers. This version was put into the environmental-test machine of the temperature of 40 degrees C, and 70% of humidity, the positive film which drew ejection and a test pattern five days after was stuck, and when changed the exposure time, it exposed, the spray of the water was carried out with the spray gun and the unexposed part was flushed in the distance of 1m with 4kw ultrahigh pressure mercury lamp, the test pattern image formed by the

hardened film was obtained. The pattern part of this image was observed and the omission nature of the pattern in the proper exposure time was observed.

Assessment: O ... The minimum resolvable line breadth was the same.

\*\* ... The minimum resolvable line breadth increased by less than 25 micrometers.

x ... The minimum resolvable line breadth increased 25 micrometers or more.

[0049] According to the conventional method of the [proper exposure-time] screen version creation, it applied to 150 meshes of polyester at the thickness of 15 micrometers, and the positive film which drew the test pattern was stuck, and when changed the exposure time, it exposed, the spray of the water was carried out with the spray gun and the unexposed part was flushed in the distance of 1m with 4kw ultrahigh pressure mercury lamp, the test pattern image formed by the hardened film was obtained. The pattern part of this image was observed and the place where the line breadth of the emulsion on a table and a background is almost the same was made into the proper exposure time.

[0050] The version used for [omission sex-test] proper exposure-time calculation was used, and the minimum line breadth which can resolve the pattern in the proper exposure time was observed and determined.

[0051] According to the conventional method of the [waterproof swelling test] screen version creation, it applied to 150 meshes of polyester at the thickness of 15 micrometers, and the 30x30mm grid positive film was used, and when it exposed in the proper exposure time of the above-mentioned calculation, the spray of the water was carried out with the spray gun and the unexposed part was flushed in the distance of 1m with 4kw ultrahigh pressure mercury lamp, the image formed by the hardened film was obtained. The image was cut to the 30x30mm intercept along with the pattern part, and the waterproof swelling test was presented.

The test-method trial intercept was dried at 40 degrees C for 24 hours, and the gravimetry (W0) was performed. After dipping this intercept in water at a room temperature for 24 hours, the gravimetry (W1) was performed. Moreover, the gravimetry (W2) of a 30x30mm screen was also performed.

$$\text{耐水膨潤率 (\%)} = \frac{W_1 - W_0}{W_0 - W_2}$$

[0052] [Existence of ink stain resistance (color contamination trial by reactive dye)]

The brackishwater which includes the color mixing CMC for sodium carbonate and caustic alkali of sodium is added, and it is Color Brill. Red was dissolved and the color contamination trial was presented.

The color sizing agent was applied to the contamination test-method screen version about 1mm in 2g and thickness, and it stopped from both sides with the pet film, and in ordinary temperature, after 3-hour neglect, rinsing desiccation was carried out and color contamination was observed.

Assessment judging O: Color contamination is completely nothing. \*\*: Color contamination is accepted slightly.

x: Color contamination is accepted.

[0053] [Abrasion resistance test]

Equipment against which a version is ground while put the waste cloth of white knitted fabric on the friction part of the grinding equipment which can apply a load at the head of a testing device, a solvent is made to always permeate a waste cloth, and it is the same period and going.

\*\* \*\*\*\* heavy: -- 2kg/cm2 grinding rate: -- 38 round trips / 60sec times number: -- 40,000 times stroke: -- 170mm assessment judging O: -- the trace of x:grinding that the trace of grinding is not observed is observed.

[0054] In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example 2 still pyridinium radical, block isocyanate (coronate 2513 made from Japanese Polyurethane Industry) 35g and vinyl acetate emulsion (product made from Hoechst Composition MA-206) 240g were mixed, the liquefied photopolymer constituent was created in

them, and the version for screen-stencil was created and evaluated like the example 1 in them. The result is shown in a table 1.

[0055] The polyvinyl alcohol water solution which added the example 3 still pyridinium radical (polymerization degree 1700 and 88% of saponification degrees) To 100g of solid content, 12% Block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g, Vinyl acetate emulsion (Hoechst composition MA-206) 240g, As photopolymerization initiator diethyl thioxan ton (KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g, and a polymerization promotor 7g emulsification and mixing of the acrylate oligomer ( TMPTA made from New Nakamura Chemistry) which carried out dissolution mixing of the 0.1g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds were done, the liquefied photopolymer constituent was created, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[0056] Block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g, vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g, and 5g of 10% diazo water solutions were mixed in 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example 4 still pyridinium radical, the liquefied photopolymer constituent was created, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[0057] In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example 5 still pyridinium radical, block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g, Vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g, As photopolymerization initiator diethyl thioxan ton ( KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g, and a polymerization promotor Acrylate oligomer ( TMPTA made from New Nakamura Chemistry) 7g which carried out dissolution mixing of the 0.1g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds was emulsified and mixed, and the liquefied photopolymer constituent was created. 5g of diazo water solutions was mixed 10% to the photopolymer constituent, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[0058] Block isocyanate (coronate 2507 made from Japanese polyurethane industry) 35g, vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g, and 5g of 10% diazo water solutions were mixed in 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example 6 still pyridinium radical, the liquefied photopolymer constituent was created, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[0059] 100g (water solution compounded in the example 3 of manufacture) of polyvinyl alcohol water solutions which added the example 7 still kino RIUMU radical -- block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g -- the place which was mixed and was stirred for 10 minutes by the homomixer -- the milk of thin yellow -- the white liquid (photopolymer constituent) was obtained. Using this liquefied photopolymer constituent, according to the conventional method of the version creation for screen-stencil, it applied to 150 meshes of polyester at the thickness of 15 micrometers, the positive film which drew the test pattern was stuck, and it exposed by distance 1M with 4kw ultrahigh pressure mercury lamp, and when the spray of the water was carried out with the spray gun and the unexposed part was flushed, the test pattern image formed by the hardened film was obtained. This image (version) was put into hot blast oven, and 180 degrees C and heat-treatment for 90 minutes were performed. The version for screen-stencil after heat-treatment is evaluated, and the result is shown in a table 1.

[0060] Mixed emulsification of imino group mold BUTOOKISHI melamine (product M-508 made from Mitsui SAITEKKU) 28g which contains xylene 10g in 100g (polymerization degree 1700, 88% of saponification degrees, 12% of solid content) of polyvinyl alcohol water solutions which added the example 8 still pyridinium radical, and the vinyl acetate emulsion (Hoechst composition MA-206) 220g was carried out, the calcium-hydroxide saturated water solution adjusted to pH6.0, and the liquefied photopolymer constituent was created. The same approach as an example 1 created and estimated the

version for screen-stencil using this liquefied photopolymer constituent. The result is shown in a table 1.

[0061] The polyvinyl alcohol water solution which added the example 9 photopolymer constituent still pyridinium radical (polymerization degree 1700 and 88% of saponification degrees) To 100g of solid content, 12% Block isocyanate (coronate 2507 made from Japanese Polyurethane Industry) 35g, Vinyl acetate emulsion (Hoechst composition MA-206) 240g, As photopolymerization initiator diethyl thioxanion ( KAYACURE[ by Nippon Kayaku Co., Ltd.] DETX) 0.25g, and a polymerization promotor 7g emulsification and mixing of the acrylate oligomer ( TMPTA made from New Nakamura Chemistry) which carried out dissolution mixing of the 0.2g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds were done, and the liquefied photopolymer constituent was created.

[0062] With the rotary screen printing above-mentioned liquid-like photopolymer constituent, it printed by creating the rotary screen version according to the following process.

(1) Wash and rinse the rotary screen cylinder-TS screen 125 (product [ made from Tree Sculpture ], and diameter 640mmphi, die length of 2,000mm, 125 meshes) manufactured by the emulsion spreading electroforming method with neutral detergent, and dry with 40-degree C hot air drying equipment. The dry cylinder was adjusted to installation and a ring-like bucket at the automatic spreading machine (Stoke AC-2000 mold), the above-mentioned photopolymer constituent was adjusted to the viscosity of 500cps / 25 degrees C, and 350g was supplied. It applied to upper part twist lower part by spreading time amount 16 minutes and 40 seconds / 1 time.

(2) \*\* The above-mentioned rotary screen cylinder which applied the \*\*\*\*\* constituent is looked like [ hot air drying equipment ] in the state of length, and 40 degrees C dries for 1 hour.

(3) Open The rotary screen cylinder which applied and dried the optical photopolymer constituent is put on an exposure machine. The film for images is twisted, a part for the connecting portion of a pattern is doubled, and it fixes with a Scotch tape (trademark). Succeedingly with an exposure machine (Stoke NEW-EP -2000) in 3kw metal halide lamp and the distance of 300mm Letting an exposure aperture pass and rotating the transit time 6 minutes and 30 second / 1 round trip of the light source, and a rotary screen cylinder 20 second / 10, it was made to go two times and exposed.

(4) \*\* Immediately after dipping an image rotary screen cylinder in a cistern for 3 minutes, after developing negatives with the developing machine (ADmade from Tree Sculpture- 2000) of a rotating type and an internal spray mold, a rotary screen cylinder is taken out, and with a water spray, the inside-and-outside section is washed, it carries out every length indoors, water is cut for 10 minutes, and it dries for 40 degrees C / 30 minutes with hot air drying equipment.

(5) The rotary screen cylinder was put into the hot blast circulation drying furnace heated by 40 degrees C of heat treatments, temperature up was carried out to 180 degrees C, and heat treatment was performed for 90 minutes at 180 degrees C.

(6) Mark The version was attached in \*\*\*\*\* and the cheesecloth was printed 10,000m.

Printing machine : rotary printing machine (R-200 by TOSHIN KOGYO CO., LTD. mold)

Printing ink: The emulsion paste containing reactive dye (seven sorts of seven colors)

Print : cheesecloth print speed : 50 m/min printing result is shown in a table 2. Consequently, even if the rotary screen version manufactured from the photopolymer constituent of elegance conventionally using the dichromate of the present marketing and the printing result more than equivalent are obtained and it does not use dichromate, safety is high, and a photopolymer constituent without environmental destruction can be offered.

[0063] After rinsing the rotary screen cylinder after 10,000m printing of existence of ink stain resistance, it dried and the stain resistance of ink was observed.

O : there is no color contamination. x: Color contamination is accepted.

After rinsing the rotary screen cylinder after 10,000m printing of destructive of the photopolymer film of a version, it dried and wear of deemulsification and the edge section was observed. Wear was judged by whether the thickness of the rotary screen cylinder after printing is decreasing by measurement of thickness.

O : there are not deemulsification and wear. x: Deemulsification and wear are accepted.

The print at the time of 10,000m printing of blots of a printing image was observed.

O : the borderline of a color and a color has clarified.

x: The borderline of a color and a color does not clarify by blot.

It placed, and after rinsing the rotary screen cylinder after 10,000m printing of reuses of a version, it dried, 5,000m printing was performed again, and it observed about the existence of contamination of ink, and emulsion destruction of a version. The assessment approach is the same as the above.

[0064] Screen-stencil was created like the example 1 using the photopolymer constituent created by the same approach as example 10 example 3. Next, it irradiates, moving by conveyor which can carry out automatic migration while setting far-infrared irradiation equipment (far-infrared heater 500 with a general-purpose reflecting plate W 6, heater skin temperature of about 500 degrees C) to parallel for this version for SUGU wood printing and keeping the distance of a far-infrared heater side and the version for screen-stencil at about 100mm. The skin temperature of the photopolymer constituent layer of the version for screen-stencil at that time is 180 degrees C. It irradiated for 3 minutes and passing speed 100 mm/min estimated the obtained version for screen-stencil according to the following approach. As the result was shown in a table 3, effectiveness equivalent to heat treatment by hot blast was acquired.

(1) It applied to the waterproof expansion test of the waterproof expansion test example 1 correspondingly, and carried out and evaluated.

(2) It applied to the abrasion resistant test of the abrasion resistant test example 1 correspondingly, and carried out and evaluated. A solvent uses water and TAPEN.

(3) It applied to the stain resistance trial of the ink of the existence example 1 of the stain resistance of ink correspondingly, and carried out and evaluated.

(4) Peel strength was measured for the bond strength of the screen pasted up on the frame and the adhesion-test version frame (construction material aluminum) of a screen with adhesives 180 degrees with S-autograph 500 mold by Shimadzu Corp., and discoloration of the adhesives at that time was observed.

[0065] 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example of comparison 1 still pyridinium radical was used as sensitization liquid, and the screen-stencil version was created and evaluated like the example 1. The result is shown in a table 1.

[0066] In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example of comparison 2 still pyridinium radical, vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g was mixed, sensitization liquid was created in them, and the version for screen-stencil was created and evaluated like the example 1 in them. The result is shown in a table 1.

[0067] 7g emulsification and mixing of the acrylate oligomer (TMPTA made from New Nakamura Chemistry) which carried out dissolution mixing of the 0.1g (KAYACURE[ by Nippon Kayaku Co., Ltd. ] EPA) of the amine compounds at 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example of comparison 3 still pyridinium radical as photopolymerization initiator diethyl thioxan ton (KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g and a polymerization promotor are done, and it is [0068]. In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example of comparison 4 still pyridinium radical, vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g and 10g of 10% diazo water solutions were mixed, sensitization liquid was created in them, and the version for screen-stencil was created and evaluated like the example 1 in them. The result is shown in a table 1.

[0069] In example of comparison 5 example 9, it carried out like the example 9 except having carried out using the sensitization liquid of a dichromate mold as sensitization liquid. The result is shown in a table 2.

[0070] In example of comparison 6 example 10, it carried out like the example 10 except having not processed far infrared rays. The result is shown in a table 3.

[0071]

[A table 1]

表 1	成分	成分名	実 験 例								比 較 例			
			1	2	3	4	5	6	7	8	1	2	3	4
分 散 媒	必須成分	実験性高含有部分酸化樹脂ビニル重合体 スチリルポリジニウム塩 スチリルキノリウム塩	100	100	100	100	100	100	100	100	100	100	100	100
分 散 媒	任意成分	ジアソ樹脂 (10%溶液)				5	5	5						10
分 散 媒	溶解性化合物	アロクイソシアネート化合物 コロネート 2513 2507	35	35	35	35	35	35	35					
分 散 媒	放射線硬化性化合物	放射線硬化性化合物 ブチロールメラミン								28				
分 散 媒	任意成分	ポリ酢酸ビニル重合体		240	240	240	240	240		220		240		240
分 散 媒	任意成分	エチレン性不飽和基含有化合物 エトキシメチルプロパノアクリレート 重合開始剤			0.2		0.2						0.2	
評価項目	紫外線の 安定性	紫外線の 安定性	○	○	○	△	△	△	○	△	○	○	○	△
評価項目	露光時間 (秒)	露光時間 (秒)	80	15	25	30	40	30	50	15	75	15	80	30
評価項目	抜け性 P150S (μm)	抜け性 P150S (μm)	100	75	50	50	50	50	120	75	200	100	150	50
評価項目	耐水膨張率 (%)	耐水膨張率 (%)	7.4	6.0	5.4	5.5	5.2	5.4	7.8	3.8	255.8	40.5	148.5	38.7
評価項目	インキ汚染性の有無	インキ汚染性の有無	○	○	○	○	○	○	○	○	×	×	×	×
評価項目	耐摩耗性 水-ベンゼン	耐摩耗性 水-ベンゼン	○	○	○	○	○	○	○	○	×	×	×	×

[0072]

[A table 2]



表 2

		実 施 例 9	比 較 例 5 従来品 (重クロム酸塩タイプ)
7色印刷後のインキ汚染性 (10,000m)		○	○
版の乳剤破壊		○	○
印刷物のしみ、汚染		○	○
置き版 の 再使用	インキ汚染性の有無 (5,000m)	○	○
	版の乳剤破壊	○	○

[0073]

[A table 3]

表 3

			実 施 例 10	比 較 例 6
遠赤外処理の有無			有	無
評 価 結 果	耐水膨潤率		5.3	39.0
	インキ汚染性		○	×
	耐摩	水	○	×
	耗性	ターペン油	○	×

[0074]

[Effect of the Invention] Such a photopolymer constituent of this invention from having used the cross-linking compound which has the above-mentioned functional group as a dispersoid While making insolubility make it water further by combining with hydrophilic radicals, such as an OH radical which remains in the vinyl acetate polymer saponification object beyond saponification degree 50 mol % with which optical bridge formation of the dispersion-medium component was carried out, and decreasing a hydrophilic radical Since a bridge is constructed with the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out, and it is unified and can be made to insolubilize further, the sensitization resin layer in which the image of the version for screen-stencil obtained was formed can show a very high water resisting property, organic solvent nature, and print durability. Moreover, after exposing and developing the water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical of a dispersion-medium component, or a styryl kino RIUMU radical beyond saponification degree 50 mol % and forming an image, an exact image can be formed from hardening a cross-linking compound. Furthermore, the photopolymer constituent which does not use dichromate and which is excellent in safety and does not have environmental destruction can be offered.

[Translation done.]



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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, in order for sensitization liquid and the film using dichromate to have toxicity in hexavalent chromium, to use it industrially and to have to carry out fully in consideration of environmental destruction of the wastewater at the time of platemaking, recovery of a used product, etc., operation industrial as a matter of fact is difficult for the actual condition. However, in textile printing using a rotary screen, since the water resisting property and solvent resistance which were excellent much more are required from the engine performance of the equipment, the photopolymer constituent with which current consists of the saponification object, the polyvinyl acetate emulsion, and dichromate of polyvinyl acetate is used.

[0004] On the other hand, although what shows a good water resisting property and solvent resistance like the above-mentioned dichromate as for sensitization liquid and the film using diazo resin was obtained, sensitization liquid and the film which added diazo resin in sensitization liquid had large aging, and since the hardening image of the stable quality was hard to be obtained, just before applying sensitization liquid to a screen mesh, they had to add diazo resin in sensitization liquid. For example, what mixed diazo resin and sensitization liquid will affect an image in one week. Moreover, since a dark reaction occurs, even if it does not make what was dried after applying the mixture of diazo resin and sensitization liquid expose, crosslinking reaction arises in two - three weeks, and it has influence on an image. Therefore, whenever it applies sensitization liquid to a screen mesh, in order to have to prepare the diazo resin of a fixed rate in sensitization liquid and to have to add in it, time amount had a fault, such as being inferior to starting workability, in film production. Furthermore, the photopolymer constituent which is excellent in the water resisting property improved further and in which water development is possible is called for. Moreover, also in the flat screen-stencil currently used abundantly at general printing, it is in the inclination for water color ink to be used from safety or the trend of deenvironmental destruction as ink used at the time of printing, and sensitization liquid and a film excellent in the much more water resisting property and solvent resistance came to be called for.

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[Translation done.]

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MEANS

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[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of the above-mentioned trouble, in order for this invention person to get the version for screen-stencil excellent in a water resisting property, organic solvent nature, and print durability After making the dispersion medium which consists of a water-soluble saponification degree % [ % of 50-99 mols ] partial saponification vinyl acetate polymer which contains the optical cross-linking radical which has optical cross-linking by itself from safety or the trend of deenvironmental destruction expose and develop By making the water-insoluble nature or the poorly soluble cross-linking compound contained as a dispersoid construct a bridge with heat By decreasing the hydrophilic radical which remains in the water which carried out optical bridge formation in a poorly soluble saponification degree % [ % of 50-99 mols ] partial saponification vinyl acetate polymer, and insolubilizing a dispersion medium in water further Based on knowledge that the version for screen-stencil excellent in a water resisting property, organic solvent nature, and print durability is obtained, it comes to complete this invention.

[0006] That is, the photopolymer constituent of this invention is characterized by coming to distribute the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat into the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol %. The version for screen-stencil which is another invention of this invention It comes to form a resin layer in a screen mesh selectively. This resin layer It consists of that by which the water-insoluble nature particle over which the bridge was constructed by heat into the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out was distributed. And it is characterized by for the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out with the water-insoluble nature particle over which the bridge was constructed by this heat constructing a bridge, and unifying it. The manufacture approach of the version for screen-stencil which is another further invention of this invention In the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol % After exposing after making a screen mesh apply and dry the photopolymer constituent which comes to distribute the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat, and developing negatives, it is characterized by irradiating heating or a radiation.

[0007]

[Embodiment of the Invention] [I] Photopolymer constituent (1) Constituent (A) In the photopolymer constituent of dispersion-medium this invention, are used as a dispersion-medium component. As a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol % A styryl pyridinium radical (\*\* 1) or a styryl kino RIUMU radical (\*\* 2) is made to add to the water-soluble vinyl acetate polymer saponification object beyond saponification degree 50 mol % as a side chain.

[0008] (a) It is the vinyl acetate polymer saponification object beyond saponification degree 50 mol %

obtained by generally saponifying a vinyl acetate polymer at a rate beyond 50 mol % as a vinyl acetate polymer saponification object beyond account saponification degree of vinyl acetate polymer saponification after 50 mol %, and polyvinyl alcohol is obtained by making a saponification degree into 100-mol %. In the vinyl acetate polymer saponification object beyond saponification degree 50 mol % of this invention, saponification degree % of the polyvinyl alcohol of 100 mols is also included.

[0009] As a vinyl acetate polymer used for the vinyl acetate polymer saponification object beyond vinyl acetate polymer above-mentioned saponification degree 50 mol %, both the gay polymer of vinyl acetate and a copolymer are included. Specifically, it is the copolymer of polyvinyl acetate, vinyl acetate, this, and a copolymerizable monomer (comonomer). As vinyl acetate and a copolymerizable monomer, on a compound and a concrete target with ethylene or an ethylene nature partial saturation radical, for example Unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, a crotonic acid, a maleic acid, a fumaric acid, and an itaconic acid Methyl acrylate, methyl methacrylate, 2-ethylhexyl AKURIRE - TO, Acrylate, such as butyl acrylate; Acrylamide, methacrylamide, Acrylamides, such as N-methylol acrylamide, N, and N-dimethyl acrylamide; A vinyl chloride, Vinyl compounds, such as a propylene, a butylene, and styrene; cationic monomers, such as dimethylaminoethyl meta-chestnut-TO, vinyl imidazo-RU, vinylpyridine, and vinyl SAKUSHIMIDO, can be mentioned. these compounds are independent -- or it can also be used together and used and, as for the content in the above-mentioned polymer, less than [ 30mol% ] is desirable.

[0010] as a vinyl acetate polymer saponification object beyond saponification degree above-mentioned saponification degree 50 mol %, the partial saponification of the vinyl acetate polymer is carried out -- making -- more than saponification degree 50 mol % -- it can consider as the 50-100-mol % and vinyl acetate polymer saponification object of the water solubility especially made into 70-99-mol % preferably preferably. And "more than saponification degree 50 mol %" means that the content of a vinyl alcohol part is a partial saponification vinyl acetate polymer saponification object beyond 50 mol %, when this vinyl acetate polymer is a gay polymer of vinyl acetate.

[0011] Water development is possible for the degree-of-polymerization above-mentioned vinyl acetate polymer saponification object beyond saponification degree 50 mol %, and it is for giving the constituent which can obtain the hardening film excellent in solvent resistance and a water resisting property after photo-curing. Moreover, as for the polymerization degree of the polymer, generally, it is preferably desirable the thing of 300-5,000 and to use the thing of 500-3,500 at the same reason.

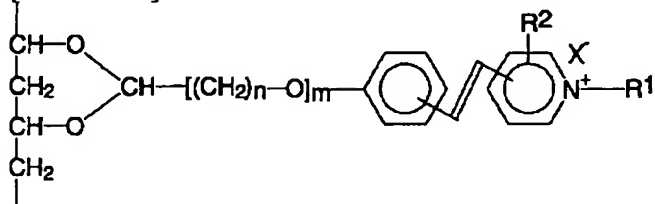
[0012] The water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical or styryl kino RIUMU radical used as a dispersion-medium component in the photopolymer constituent of this invention beyond saponification degree 50 mol % is water solubility. And it has an emulsification property or a protective colloid property for the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat, and the dispersoid which consists of a hydrophobic polymer particle used as occasion demands, and the property which is not dissolved in a common organic solvent under the usual conditions is required. Therefore, the saponification object (more than saponification degree 50 mol %) of a copolymerization object with a compound with the saponification object (more than saponification degree 50 mol %) of a vinyl acetate polymer, vinyl acetate and ethylene, or an ethylene nature partial saturation radical, polyvinyl alcohol polymers, or these derivatives are suitable. moreover -- as the derivative of a polymer saponification object -- formaldehyde, an acetaldehyde, a butyraldehyde, and benzaldehyde etc. -- the added object can be used. As for the amount of addition, less than [ 30mol% ] is desirable. Specifically, these side-chain derivatives can be mentioned, including the acetal ghost by low-grade (C1-C4) acetal ghost [ , such as formal-izing of saponification polyvinyl acetate, or butyral-izing, ] and p-benzaldehyde sulfonic-acid, beta-butyraldehyde sulfonic-acid, o-benzaldehyde sulfonic-acid, 2, and 4-benzaldehyde disulfon acid etc.

[0013] (b) Set to the photopolymer constituent of optical cross-linking basic invention, and it is a water-soluble vinyl acetate polymer saponification object beyond saponification degree 50 mol %. As the styryl pyridinium radical (\*\* 1) contained as a side chain in inside, or a styryl kino RIUMU radical (\*\* 2), it is the optical cross-linking radical which has optical cross-linking by itself. The water-soluble vinyl

acetate polymer saponification object containing the styryl pyridinium radical or styryl kino RIUMU radical used in this invention beyond saponification degree 50 mol % makes the styryl pyridinium radical (\*\* 1) or styryl kino RIUMU radical (\*\* 2) expressed with the following general formula (I) and (II) add. General formula (I)

[0014]

[Formula 1]

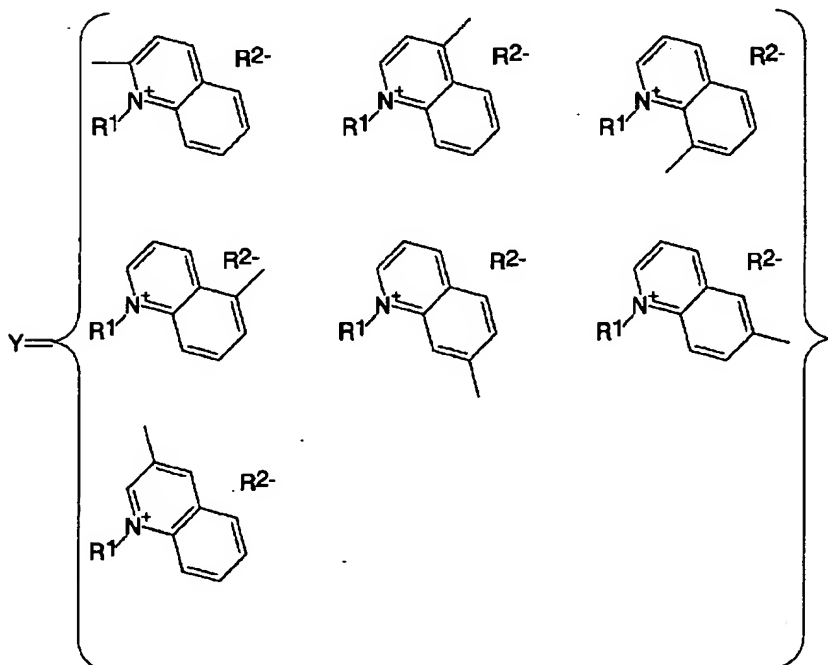
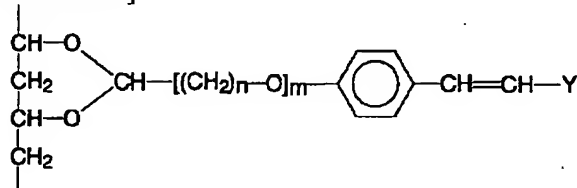


[0015] (\*\* 1)

General formula (II)

[0016]

[Formula 2]



[0017] (\*\* 2)

However, R1 shows a hydrogen atom, an alkyl group, or an aralkyl radical among the above-mentioned general formula (I) and (II), these may also include hydroxyl, a carbamoyl group, ether linkage, and an unsaturated bond, and R2 shows a hydrogen atom or a low-grade alkyl group. X - The mixture of

halogen ion, phosphoric-acid ion, p-toluenesulfonic-acid ion, or these anions is shown, and, as for 0 or 1, and n, m shows the integer of 1-6. The partial saponification vinyl acetate polymer which has the above still BAZORIUM radicals, and its manufacturing method are already known (JP,55-23163,A, JP,55-62905,A, and JP,55-62405,A each official report). the amount of addition of the styryl pyridinium radical of photodimerization nature, and a styryl quinolinium radical -- general -- 0.2-7.0-mol % -- it is 0.5-5.0-mol % preferably. There is an inclination whose image formation is fully impossible in it being under the above-mentioned range. Moreover, when the above-mentioned range is exceeded, there is an inclination for dissolved water in fuel to worsen. As for the dispersion-medium component which consists of a water-soluble vinyl acetate polymer saponification object containing these styryls pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol %, diluting bywater is common.

[0018] (B) Water-insoluble nature or a poorly soluble cross-linking compound (dispersoid)

(a) As a dispersoid which consists of the water-insoluble nature or the poorly soluble cross-linking compound used as a dispersoid component in the photopolymer constituent of cross-linking compound this invention, it is the cross-linking compound which constructs a bridge with heat. They are the compound which has a radical with active hydrogen, such as water-soluble-OH radical of the vinyl acetate polymer beyond saponification degree 50 mol % used as a dispersion-medium component by irradiating heating or a heat ray as a cross-linking compound which constructs a bridge with heat, or a polyvinyl alcohol polymer, -COOH radical and -NH<sub>2</sub>, and -SH, and the functional group which can react, and the compound which has two or more functional groups preferably. Such a functional group As an example, an aldehyde group, an isocyanate radical, an alkoxy group, a glycidyl group, an ethylene nature partial saturation radical, the amino group, and diester can be mentioned, for example.

Specifically as a compound which has such a functional group, ethylene nature partial saturation radical content compounds, such as metal chelate compound, such as dialdehyde compounds, such as alkoxy compounds, such as amino compounds, such as thiourea, a melamine, and benzoGUAMIN, a methylol-ized melamine, a BUCHIRORU-ized melamine, and methylol acrylamide, glyoxal, and a glutaraldehyde, a block isocyanate compound shown in the following, cobalt, titanium, a zirconium, and molybdenum, an acryloyl radical, a meta-acryloyl radical, S Kurile amide group, and a vinyl ether radical etc. can be mentioned Furthermore, it can be more effectively used by making these compounds live together. The photopolymer constituent which used especially the block isocyanate compound also in the compound which has these functional groups is desirable from excelling in long term stability.

[0019] The block isocyanate compound above-mentioned block isocyanate compound carries out the mask of the isocyanate radical of an isocyanate compound by the block agent (for example, compounds, such as a caprolactam which has active hydrogen, activity methylene, and an oxime), in ordinary temperature, although it is stable, if it heats (usually 120 degrees C or more), a block agent will dissociate and an activity isocyanate radical will be reproduced. As an isocyanate compound used for the above-mentioned block isocyanate compound It is what two or more isocyanate radicals have. As an example of such a compound 2, 6-tolylene diisocyanate (2, 6-tolylene diisocyanate), 2, 4 tolylene diisocyanate (2, 4-tolylene diisocyanate), 4 and 4-diphenyl methane diisocyanate, 1,5-naphthalene diisocyanate, Aromatic series diisocyanate, such as m-xylenediisocyanate and m-tetramethyl xylenediisocyanate, Methyl hexamethylene di-isocyanate, 2 and 2, 4 trimethyl hexamethylene di-isocyanate, Aliphatic series isocyanates, such as 2, 4, and 4 trimethyl hexamethylene di-isocyanate, Isophorone diisocyanate, hydrogenation 4, 4' diphenyl methane diisocyanate, Alicycle group diisocyanate, such as hydrogenation m-xylenediisocyanate, Triphenylmethane triisocyanate, polymethylene polyphenyl isocyanate, Polyfunctional aromatic series isocyanate compounds, such as the trimethylol propane adduct object and isocyanurate object of tolylene diisocyanate, polymeric methane diisocyanate, and other prepolymer isocyanates, etc. can be mentioned. the block isocyanate compound which carried out the mask to these isocyanate compounds by the block agent is independent -- or it can use together and use. As for the above-mentioned block isocyanate compound, it is desirable that it is the emulsification block isocyanate compound which carried out emulsification distribution into the dispersion-medium component which consists of a water-soluble vinyl acetate polymer

saponification object containing the styryl pyridinium radical in a photopolymer constituent or a styryl kino RIUMU radical beyond saponification degree 50 mol % and which was distributed minutely. Consequently, the stable photopolymer constituent is obtained. Moreover, it may mix with other compounds, the compound which is not emulsified if independent may also be made to emulsify, and you may use it further, dissolving in an organic solvent (hydrophobicity is desirable). It is not necessary to be the compound which the polymer and prepolymer which are compatible in the block isocyanate compound emulsified and distributed could be mixed and used into the dispersion-medium component, and such a polymer and a prepolymer not necessarily had - OH radical, -COOH radical and two -NH(s), - sulfhydryl group, etc., and was rich in an isocyanate radical and reactivity. However, what has good emulsification / distribution property is desirable in water at poor solubility.

[0020] (b) The cross-linking compound which constructs a bridge with the water-insoluble nature or the poorly soluble heat used as a dispersoid component in the water-insoluble nature of a dispersoid component, or the photopolymer constituent of poorly soluble this invention From it having to distribute in the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical or styryl kino RIUMU radical contained in the photopolymer constituent of this invention beyond saponification degree 50 mol % It is important that they are water-insoluble nature or a poorly soluble thing. Moreover, the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat First, photocuring of the dispersion-medium component in a photopolymer constituent is carried out by making a photopolymer constituent expose through a mask film at an exposure process. Furthermore, after carrying out dissolution clearance of the unexposed dispersion-medium component and making an image form by carrying out water development, in order to stiffen a dispersoid component by irradiating heating or a heat ray at heating or a heat radiation process at a dispersoid component It is important that a dispersoid component dissolves by water and is not extracted in the development process at the time of the image formation which is a before process.

[0021] rack a pons -- by using the cross-linking compound which has the above-mentioned functional group as such a dispersoid While making it water further at insolubility by combining with hydrophilic radicals, such as an OH radical which remains in the vinyl acetate polymer saponification object beyond saponification degree 50 mol % with which optical bridge formation of the dispersion-medium component was carried out, and decreasing a hydrophilic radical Since a bridge is constructed with the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out, and it is unified and can be made to insolubilize further, the sensitization resin layer in which the image of the version for screen-stencil obtained was formed can raise a water resisting property, organic solvent nature, and print durability further.

[0022] (C) The dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical or styryl kino RIUMU radical contained in the photopolymer constituent of blending-ratio-of-coal this invention beyond saponification degree 50 mol %, The blending ratio of coal with the dispersoid which consists of a cross-linking compound which constructs a bridge with the water-insoluble nature or the poorly soluble heat distributed in this dispersion medium the solid content 100 weight section in an aqueous dispersion medium -- receiving -- a cross-linking compound -- general -- the 10 - 500 weight section -- desirable -- the 30 - 400 weight section -- it is especially blended at a rate of the 50 - 300 weight section preferably. The inclination which is not enough is in an improvement of a deck watertight luminaire and solvent resistance under in the above-mentioned range. Moreover, when the above-mentioned range is exceeded, there is an inclination emulsion stability becomes [ an inclination ] easy to carry out a separation deposit bad. Furthermore, it coats, and the sensitization resin film after desiccation has a strong tuck, and has the inclination for the bleeding of a cross-linking compound to become intense.

[0023] (2) Although the photopolymer constituent of constituent this invention of arbitration consists of the above-mentioned constituent fundamentally, it is desirable to blend the compound which has an ethylene nature partial saturation radical containing the hydrophobic polymer particle shown below as a component of arbitration, a photoinitiator cross linking reagent, and a photopolymerization initiator.

[0024] (A) A water resisting property can be further raised by making the dispersoid which consists of a hydrophobic polymer particle into the hydrophobic polymer particle above-mentioned photopolymer constituent contain. The dispersion liquid of the giant-molecule polymer which the water-insoluble nature giant-molecule distribution object had the emulsion obtained by the inside of a polymerization process distributed by remaining as it is, and was distributed [ polymer / giant-molecule ] by the main dispersion medium in water and water are used. It is easily mixable in the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol %, and the dispersion liquid of the giant-molecule polymer containing such a hydrophobic polymer particle can be used if neither condensation nor precipitate is caused. As for especially the photopolymer constituent with which such a hydrophobic polymer particle was distributed, it is desirable that 50 micrometers or less of mean particle diameter of a hydrophobic polymer particle are 15 micrometers or less. It is desirable to the solid content 100 weight section in a photopolymer constituent 5 - 95 weight section and to make the loadings of such a hydrophobic polymer particle component into 20 - 85 weight section preferably as solid content. When there is an inclination for the waterproof improvement effectiveness to the hardening film to be unable to show up [ the loadings of a hydrophobic polymer particle component ] easily under in the above-mentioned range and the above-mentioned range is exceeded, there is an inclination for an image with sufficient repeatability with bad development nature to be hard to be obtained. The dispersion liquid of the macromolecule polymer which such a hydrophobic polymer particle component had the emulsion obtained by the inside of a polymerization process distributed by remaining as it is, and was distributed [ polymer / macromolecule ] by the main dispersion medium in water and water are used. The high molecular compound and naturally-occurring-polymers compound which were compounded are sufficient as these hydrophobic polymer particle components. printing the effectiveness of the hydrophobic polymer particle component of this invention improves the water resisting property of the formed image, and using improvement in definition, and water color ink and the aquosity paste of a photo-curing image as the result -- improvement relation in print durability is carried out.

[0025] As the above-mentioned hydrophobic polymer particle, they are polyvinyl acetate, vinyl acetate / ethylene copolymer, and vinyl acetate / acrylic ester copolymer (as acrylic ester here), for example. for example, there are a methyl acrylate, 2-ethylhexyl acrylate, etc. An acrylic-acid (meta) polymer, styrene / butadiene copolymer, a methyl methacrylate / butadiene copolymer, Acrylonitrile / butadiene copolymer, a chloroprene polymer, an isoprene polymer, a polyvinyl chloride, a polyvinylidene chloride, polystyrene, silicone resin, polyethylene, polyurethane, a fluororesin, etc. can be mentioned. These hydrophobic polymer particle can mention the polyvinyl acetate emulsion obtained more in process, ethylene and a vinyl acetate copolymer emulsion, a vinyl acetate acrylic copolymer emulsion, ethylene and the polymerization vinyl acetate acrylic copolymerization emulsion of 3 yuan, a vinyl chloride and a vinyl acetate emulsion, an acrylic emulsion, a styrene butadiene latex emulsion, an MBR latex emulsion, an acrylonitrile-butadiene rubber latex emulsion, a chloroprene rubber-latex emulsion, a vinylidene-chloride emulsion, etc. As synthetic macromolecule dispersion, polyethylene dispersion, polyolefine ionomer dispersion, urethane ionomer dispersion, etc. are useful. Moreover, what distributed synthetic macromolecule pulverized coal and purification starch can be used.

[0026] (B) Although the photopolymer constituent of photoinitiator cross linking reagent this invention can obtain enough hardening images by the optical cross-linking radical which has optical cross-linking contained in an aquosity dispersion-medium component, it can obtain the hardening image which was further excellent by adding a photoinitiator cross linking reagent (diaz resin) further. However, in adding only a photoinitiator cross linking reagent, the preservation stability of a photopolymer constituent gets worse, or there is also a fault to which photosensitivity falls. As such a diazo resin compound, a dimethoxy diphenyl ether condensate, the paraformaldehyde condensate of a 4-diazo 3-methoxy diphenylamine, or paraformaldehyde condensate [ of a p-diazo diphenyl amine ] or 4, and 4', 4' dimethoxy diphenyl ether condensate can be mentioned. Furthermore, a new diazo compound given in JP,5-125031,A etc. is useful. When making diazo resin contain, it is desirable to the solid content 100



weight section in a photopolymer constituent 0.1 - 4 weight section and to contain at a rate of the 0.2 - 2.5 weight section preferably as solid content.

[0027] (C) If a photopolymerization initiator is used for a compound with the compound ethylene nature partial saturation radical which has an ethylene nature partial saturation radical containing a photopolymerization initiator, dissolving or mixing, the polymerization of this mixture will be carried out by light, and it will be macromolecule-ized. Moreover, an aqueous dispersion-medium component and a dispersoid, and graft polymerization bridge formation are also started simultaneously, and the deck watertight luminaire and the solvent resistance of a hardened material are raised. a compound with an ethylene nature partial saturation radical -- carrying out -- it is insoluble in water and what can be easily emulsified in a component (A) solution is desirable.

[0028] the compound which has an ethylene nature partial saturation radical -- it is the compound with which it has one or more ethylene nature partial saturation radicals, such as an acryloyl radical, a meta-acryloyl radical, an allyl group, a vinyl ether radical, an acrylamide radical, and a meta-acrylamide radical, and an insoluble or poorly soluble thing has an acryloyl radical and one or more meta-acryloyl radicals preferably desirable especially in water as a compound which has such an ethylene nature partial saturation radical. As such a compound, specifically For example, pen TAERISURITORUTORI (meta) acrylate, Pentaerythritol tetrapod (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, Trimethylolethane tri(metha)acrylate, dipentaerythritol hexa (meta) acrylate, Ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Tetra-ethylene GURIKORUJI (meta) acrylate, hexa ethylene GURIKORUJI (meta) acrylate, a jib -- ROMUHEO pentyl GURIKORUJI (meta) acrylate, 2, and 8 jib -- hawk alcoholic multiple-valued acrylate, such as ROM neopentyl GURIKORUJI (meta) acrylate, -- 2 and 2-bis(4-meta-KURIROKISHI ethoxy phenyl) propane, 2, and 2-(4-acryloxy ethoxy phenyl) propane, Epoxy acrylate, such as an acrylic acid of the epoxy resin of bisphenol A and an epichlorohydrin system, or a methacrylic-acid addition product, An addition product with the acrylic acid of trimethylolpropane triglycidyl ether or methacrylic acid, the urethane (meta) acrylic compound obtained at the reaction of TORIHEKISA methylene G SOSHINETO and the acrylic (meta) mono-acid ester of dihydric alcohol are mentioned. These compounds can use together and use independent or two sorts or more. As for the photopolymer constituent with which the compound which has an ethylene nature partial saturation radical containing such a photopolymerization initiator was distributed, it is desirable that 20 micrometers or less of mean particle diameter of the compound which has an ethylene nature partial saturation radical are especially 10 micrometers or less. It is desirable to the solid content 100 weight section in a photopolymer constituent 0.5 - 70 weight section and to make preferably into 1 - 50 weight section the loadings of the compound component which has such an ethylene nature partial saturation radical. When there is an inclination for the waterproof improvement effectiveness at the time of development to be unable to show up [ the loadings of the compound component which has an ethylene nature partial saturation radical ] easily under in the above-mentioned range and the above-mentioned range is exceeded, there is an inclination for an image with sufficient repeatability with bad development nature to be hard to be obtained.

[0029] In order to make the photopolymerization initiator above-mentioned polymerization nature compound react promptly by optical exposure, it is common to add a photopolymerization initiator. As for such a photopolymerization initiator, it is desirable that dissolve or dissolve in the above-mentioned polymerization nature compound, and homogeneity is mixed. As such a photopolymerization nature initiator, thioxan ton derivatives, such as anthraquinone, such as a benzophenone, benzoin alkyl ether, a MIHIRAZU ketone, benzyl, the benzyl dialkyl ether, and TASHARU butyl anthraquinone, a chloro thioxan ton, and an isopropyl thioxan ton, etc. are mentioned. Furthermore, photopolymerization accelerators, such as p-dimethylamino isoamyl benzoate ester and p-dimethylamino ethyl benzoate ester, may be mixed. These are effective when speeding up the polymerization cure rate at the time of using a benzophenone system and a thioxan ton system. Generally the above-mentioned photopolymerization nature initiator is blended at a rate of 1 - 10 weight section to the compound 100 weight section which has an ethylene nature partial saturation radical.

[0030] (D) Although it is desirable that the above-mentioned arbitration component is blended as for the

photopolymer constituent of other arbitration component this inventions, it can add further the additive component usually contained in this kind of photopolymer constituent to arbitration. As an additive component of such arbitration, the solid content 100 weight section in the above-mentioned photopolymer constituent is received, for example. The emulsion stabilizer below the 0.5 weight section As a solubilizing agent of the compound containing the cross-linking compound and the ethylene nature partial saturation radical which can be photopolymerized which constructs a bridge with heat The coloring agent which makes images, such as a color and a pigment, legible for an organic solvent without the water and the miscibility below 30 weight sections further, a defoaming agent, etc. can be added within limits usually added to these 100 weight sections. Moreover, inorganic fine particles can be added by within the limits below 30 weight sections to the solid content 100 weight section in a photopolymer constituent as an extending agent or a tack inhibitor.

[0031] (3) In order to obtain the photopolymer constituent of this invention from the preparation above-mentioned constituent and arbitration component of a photopolymer constituent, it can usually prepare by the approach shown below.

The manufacture partial saponification vinyl acetate polymer of a photosensitive polymer is dissolved in water, the compound containing a styryl pyridinium radical or a styryl kino RIUMU radical is dissolved in this solution, it adds and a phosphoric acid is made to react further. The photosensitive polymer water solution which consists of a partial saponification polyvinyl acetate polymer with which the styryl pyridinium radical or styryl kino RIUMU radical which becomes the column filled up with anion \*\*\*\*\* from the viscous liquid of through and thin yellow added this reaction mixture is obtained.

[0032] Milk The photopolymer constituent of this invention is obtained by adding the cross-linking compound which constructs a bridge with heat, or the cross-linking compound which constructs a bridge with the heat which mixed the little organic solvent used if needed in the photosensitive polymer water solution of-izing \*\*, and stirring and emulsifying with a kneader, a homomixer screw-type agitator, etc. in it.

[0033] The photopolymer constituent of this invention improved further is obtained by adding and emulsifying combination of an arbitration component, and also the photopolymerization nature compound which carried out dissolution mixing of a photopolymerization initiator or the photopolymerization accelerator if needed, and adding the diazo compound which is a photoinitiator cross linking reagent, and mixing [ \*\*\*\* / mixing hydrophobic giant-molecule polymer dispersion liquid, and a coloring agent and a defoaming agent ] if needed. In addition, it is not fixed to the above-mentioned sequence and the addition sequence of each component can change addition sequence in the range which the problem at the time of mixing of condensation, separation, a deposit, etc. does not produce. However, since the stability of a diazo compound in the inside of a water solution is not good, the preservation stability of sensitization liquid tends to fall. Therefore, adding just before an activity is desirable.

[0034] (4) business a way -- such a photopolymer constituent of this invention It responds to various applications. Metal plates, such as aluminum, nickel, and stainless steel, [ whether it applies on the base material of arbitration, such as a synthetic-resin plate, a semi-conductor substrate, and a stone and a laminating is dried and carried out, and ] Various screen mesh (mesh, such as a polyamide, polyester, and stainless steel), Applied to a table rear face or front faces, such as a rotary screen cylinder, and were formed by drying. For example, the activity light which becomes a photopolymer ingredient with a dry thickness of 1-1000 micrometers from ultraviolet rays etc. For example, after in the case of ultraviolet rays having irradiated through the predetermined pattern with the mask etc. so that the amount of exposure energy of the wavelength the range of 300-450nm might become two or more 10 mj/cm, and stiffening an exposure part, If spray water etc. removes the part which is not hardened [ of a non-irradiating part ], a relief image or the image film will be formed. Furthermore, about this formed relief image or image film, by carrying out exposure processing of heat-treatment or a near infrared ray, far infrared rays, the microwave, etc. in a 120-200-degree C ambient atmosphere preferably, the hardening reaction of the image film advances further and 50-220 degrees C becomes the image film excellent in a deck watertight luminaire and solvent resistance. Therefore, it can use for the application of resist film,

such as the various printing versions which used such a photopolymer constituent, such as screen-stencil and Toppan Printing, and various etching resist, sandblasting etching, etc. It is desirable to use as a version for screen-stencil also in these applications.

[0035] [II] The manufacture approach of the version for screen-stencil as a desirable application of the photopolymer constituent which is the manufacture above of the version for screen-stencil, and was made and obtained is indicated in a detail below.

It responds to spreading / desiccation process application. (1) Aluminum, stainless steel, the flat screen-stencil frame which manufactured metal cylindrical raw materials, such as steel, in the square or the rectangle -- various screen mesh -- sha -- with the bucket for the flat screen versions for the flat screen version which carried out the flare or [ carrying out the laminating of the above-mentioned photopolymer constituent by predetermined thickness by repeating spreading and a desiccation process according to a conventional method ] -- or On the metal rotary screen cylinder formed by the electroforming method, with a ring-like bucket According to a conventional method, the photopolymer film with which 0.5-1,000 micrometers of 1-400 micrometers of desiccation thickness generally consist of a photopolymer constituent with a thickness of 1-200 micrometers preferably especially is formed 1 time or by repeating several times in spreading and the desiccation process of the above-mentioned photopolymer constituent. Thus, an overcoat layer can also be formed in front flesh-side both sides of the photopolymer film which consists of an obtained photopolymer constituent for this film protection. The PS plate for screen-stencil can be obtained by this. It is polyethylene about the approach and sensitization liquid which face obtaining the version for screen-stencil and apply sensitization liquid directly, Scree which applies and dries, obtains the 5-1,000-micrometer film, and applied water or sensitization liquid for this film on plastic films, such as a polyvinyl chloride and polyester There is the approach (approach called the method between [ so-called ] direct) of imprinting on - N. The photopolymer constituent of this invention can form a film by such approach.

[0036] The film which consists of a negative film or a positive film the film which becomes the screen stretched by the exposure process above-mentioned shuttering from a photopolymer constituent is minded. (2) Ultraviolet rays, By irradiating beams of light, such as a visible ray and an argon laser, and exposing them The dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing the styryl pyridinium radical in the photopolymer layer by the side of the rear face of the part which the image is drawn on this film and does not penetrate light, or a styryl kino RIUMU radical beyond saponification degree 50 mol % serves as unexposed, and does not harden. It can harden by exposing the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object beyond saponification degree 50 mol % which, on the other hand, contains the styryl pyridinium radical in the photopolymer layer by the side of the rear face of a part where the image is not drawn on this film, or a styryl kino RIUMU radical, and carrying out lifting light bridge formation of the photoreaction, and a latent-image image can be made to form in the photopolymer layer of this part. The output of 1-15kW, exposure can use the light source of a 2-6kW ultrahigh pressure mercury lamp, a high-pressure mercury-vapor lamp, a metal halide content high-pressure mercury-vapor lamp, etc. preferably, and, generally is preferably performed by irradiating for [ 5 seconds - ] 5 minutes preferably for [ 3 seconds - ] 20 minutes from distance (0.2-1.5m) 0.1-2m.

[0037] In the photopolymer layer which has this exposed latent-image image, \*\*\*\*\* (3) Water, an alkali water solution, Or by carrying out dissolution clearance of the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object beyond saponification degree 50 mol % which contains the styryl pyridinium radical in the photopolymer layer of an unexposed part, or a styryl kino RIUMU radical by spraying an acid water solution with a spray By removing the dispersoid which consists of the water-insoluble nature or the poorly soluble cross-linking compound distributed in this dispersion medium, the version for screen-stencil with which the image was formed is obtained.

Generally development is performed for 1 - 10 minutes. However, although it has the water resisting property from which the photopolymer layer of the version for screen-stencil obtained here is poorly soluble, and is equal to a development activity to water, and sufficient image repeatability is acquired, since printing which used water color ink and printing paste cannot be borne, in order to give the further

water resisting property, in the invention in this application, the following heating down stream processing is indispensable.

[0038] (4) Heating down stream processing (a) Although about 40 degrees C usually dries in order to dry the version for screen-stencil obtained by the heat-treatment above-mentioned development generally Generally in this invention, 100-220 degree C of 50-220 degree C of \*\*\*\*\* especially given to heating down stream processing at the temperature of 130-200 degrees C preferably are preferably important as the temperature from which said cross-linking compound higher than the above-mentioned drying temperature starts crosslinking reaction, and concrete heat-treatment temperature. Generally as time amount of such heat-treatment, it is 1 - 2.5 hours preferably for 0.5 to 4 hours. Such heat-treatment is performed by irradiating heating or a heat ray. As for the above-mentioned heating, it is common to be performed by hot blast heating furnaces, such as a drying furnace which is generally in heating furnaces, such as oven, or carries out circulation air blasting of the hot blast, etc. As the above-mentioned heat ray, a near infrared ray, far infrared rays, microwave, etc. can be mentioned.

[0039] (b) rack a pons -- by \*\*\*\*\* given to such heating down stream processing When the dispersoid which consists of the water-insoluble nature or the poorly soluble cross-linking compound currently distributed in the vinyl acetate polymer saponification object beyond [ poorly soluble ] saponification degree 50 mol % reacts to the water which carried out optical bridge formation in the photopolymer layer of the version for screen-stencil, macromolecule-ize, or While making a dispersoid into a water-insoluble nature particle by constructing a bridge, this water-insoluble nature particle reacts with the hydroxyl group which remains in the vinyl acetate polymer saponification object beyond saponification degree 50 mol % which carried out optical bridge formation, and decrease, and insolubilize [ water-] or grit [ difficulty-] the hydroxyl group which is a hydrophilic radical, or It can be made to insolubilize further much more by reacting with a hydroxyl group by constructing a bridge with the vinyl acetate polymer saponification object beyond saponification degree 50 mol % which carried out optical bridge formation, and considering as a huger molecule.

[0040] [III] Version for screen-stencil (1) Style The version for screen-stencil obtained by \*(ing) thus carrying out Use the above-mentioned photopolymer constituent, apply and from being manufactured by exposure, development, heating or heat ray processing Form a resin layer in the screen mesh stretched by shuttering by fixed thickness selectively, and the image is formed. This resin layer itself is a thing in the condition of having distributed the water-insoluble nature particle over which the bridge was constructed by heat into the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out. It is constructed a bridge and unified, the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out with the water-insoluble nature particle over which the bridge was constructed by this heat is in an insoluble condition and the insoluble condition of being hard to swell at water or an organic solvent, and it has become the version for screen-stencil excellent in a water resisting property, organic solvent nature, and print durability.

[0041] (2) seed a kind -- such a version for screen-stencil becomes the thing excellent in a water resisting property, organic solvent nature, and print durability, also when it is used for the usual flat screen-stencil version and usual rotary screen cylinder which are used in case it screen-stencils using a flat screen printer or a rotary screen printing machine as a rotary screen printing version which applied and dried the photopolymer constituent. Especially the thing used especially as a rotary screen printing version which used the rotary screen cylinder is useful.

[0042] (3) business a way -- by making it slide, laying the ink for screen-stencil on the film side of the above-mentioned flat screen-stencil version, grinding this film side against a squeegee strongly, and contacting screen \*\* to a printing hand-ed, such a version for screen-stencil can make the pore of this film side able to penetrate ink, can be made to be able to put on the printing hand-ed by the side of the rear face of this film, and can print an image, an alphabetic character, etc. Specifically, it is broadly applicable to printing to the product stuck to the life to building inner package material, such as textile printing of printing of industrial components, such as a printed circuit board, or a T-shirt, a handkerchief, etc., pottery, glass, an advertising signboard, a poster and endless textile printing, and wall

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covering flooring, etc.

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[Translation done.]

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EXAMPLE

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[Example] [I] 120g (polymerization degree 1700) of 88% (example 1 of manufacture) saponification polyvinyl acetate of manufactures of a dispersion medium was dissolved in 1000g of ion exchange water. 24g of N-methyl-gamma-(p-formyl styryl) pyridinium-dimethyl sulfates was dissolved in this solution, and it reacted, having added 5g of phosphoric acids 85 more%, and stirring at 45 degrees C for 30 hours. Furthermore, the viscous liquid of through and the thin yellow of PH6.0 was created in the column filled up with anion exchange resin at reaction mixture. the result of measurement -- an N-methyl-gamma-(p-formyl styryl) pyridinium-dimethyl sulfate -- 88% saponification polyvinyl acetate -- receiving -- 1.5-mol% -- having added was checked.

[0044] (Example 2 of manufacture) It is \*\* to 15 degrees C or less after dissolving 7.5g of P-diazo diphenylamine hydrogensulfates in 15g of sulfuric acids 95%, adding paraformaldehyde 1g gradually further and stirring at 10 degrees C for 3 hours. The precipitate which added 100ml ethanol gradually with \*\*, and was obtained was filtered. Furthermore, it washed this precipitate each with 4 sufficient times by 100ml ethanol, and it dried and the diazo resin fine particles of the yellow which green cut were obtained.

[0045] (Example 3 of manufacture) 120g (polymerization degree 1700) of saponification polyvinyl acetate was dissolved in 1000g of ion exchange water 88%. 28g of N-methyl-2-(p-formyl styryl) kino RIUMU-dimethyl sulfates was dissolved in this solution, and it reacted, having added 5g of phosphoric acids 85 more%, and stirring at 45 degrees C for 30 hours. Furthermore, the viscous liquid of through and the thin yellow of PH6.0 was created in the column filled up with anion exchange resin at reaction mixture. the result of measurement -- an N-methyl-2-(p-formyl styryl) kino RIUMU-dimethyl sulfate -- 88% saponification polyvinyl acetate -- receiving -- 1.2-mol% -- having added was checked.

[0046] [II] 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the manufacture example 1 still pyridinium radical of a photopolymer constituent -- block isocyanate (coronate 2513 made from Japanese Polyurethane Industry) 35g -- the place which was mixed and was stirred for 10 minutes by the homomixer -- the milk of thin yellow -- the white liquid (photopolymer constituent) was obtained. Using this liquefied photopolymer constituent, according to the conventional method of the version creation for screen-stencil, it applied to 150 meshes of polyester at the thickness of 15 micrometers, the positive film which drew the test pattern was stuck, and it exposed by distance 1M with 4kw ultrahigh pressure mercury lamp, and when the spray of the water was carried out with the spray gun and the unexposed part was flushed, the test pattern image formed by the hardened film was obtained. Next, this image (version) was put into hot blast oven, and 180 degrees C and heat-treatment for 90 minutes were performed. Assessment of the obtained version for screen-stencil was carried out according to the following approach. The result is shown in a table 1.

[0047] Sensitization liquid was made into 25 degrees C with the [stability test of sensitization liquid] thermostat, the Brookfield viscometer was used, and measurement of viscosity was performed. The sensitization liquid was put in the bottle made from polyethylene, it put into the environmental-test machine of the temperature of 30 degrees C, and 70% of humidity, ejection and a Brookfield viscometer

were used ten days after, and the viscosity at the time of 25 degrees C was measured.

評価：○・・・粘度変化が0～5%であった。

△・・・粘度変化が5～20%であった。

×・・・粘度変化が20%以上であった。

[0048] According to the conventional method of the [stability test of film] screen version creation, it applied to 150 meshes of polyester at the thickness of 15 micrometers. This version was put into the environmental-test machine of the temperature of 40 degrees C, and 70% of humidity, the positive film which drew ejection and a test pattern five days after was stuck, and when changed the exposure time, it exposed, the spray of the water was carried out with the spray gun and the unexposed part was flushed in the distance of 1m with 4kw ultrahigh pressure mercury lamp, the test pattern image formed by the hardened film was obtained. The pattern part of this image was observed and the omission nature of the pattern in the proper exposure time was observed.

Assessment: O ... The minimum resolvable line breadth was the same.

\*\* ... The minimum resolvable line breadth increased by less than 25 micrometers.

x ... The minimum resolvable line breadth increased 25 micrometers or more.

[0049] According to the conventional method of the [proper exposure-time] screen version creation, it applied to 150 meshes of polyester at the thickness of 15 micrometers, and the positive film which drew the test pattern was stuck, and when changed the exposure time, it exposed, the spray of the water was carried out with the spray gun and the unexposed part was flushed in the distance of 1m with 4kw ultrahigh pressure mercury lamp, the test pattern image formed by the hardened film was obtained. The pattern part of this image was observed and the place where the line breadth of the emulsion on a table and a background is almost the same was made into the proper exposure time.

[0050] The version used for [omission sex-test] proper exposure-time calculation was used, and the minimum line breadth which can resolve the pattern in the proper exposure time was observed and determined.

[0051] According to the conventional method of the [waterproof swelling test] screen version creation, it applied to 150 meshes of polyester at the thickness of 15 micrometers, and the 30x30mm grid positive film was used, and when it exposed in the proper exposure time of the above-mentioned calculation, the spray of the water was carried out with the spray gun and the unexposed part was flushed in the distance of 1m with 4kw ultrahigh pressure mercury lamp, the image formed by the hardened film was obtained. The image was cut to the 30x30mm intercept along with the pattern part, and the waterproof swelling test was presented.

The test-method trial intercept was dried at 40 degrees C for 24 hours, and the gravimetry (W0) was performed. After dipping this intercept in water at a room temperature for 24 hours, the gravimetry (W1) was performed. Moreover, the gravimetry (W2) of a 30x30mm screen was also performed.

$$\text{耐水膨潤率 (\%)} = \frac{W_1 - W_0}{W_0 - W_2}$$

[0052] [Existence of ink stain resistance (color contamination trial by reactive dye)]

The brackishwater which includes the color mixing CMC for sodium carbonate and caustic alkali of sodium is added, and it is Color Brill. Red was dissolved and the color contamination trial was presented.

The color sizing agent was applied to the contamination test-method screen version about 1mm in 2g and thickness, and it stopped from both sides with the pet film, and in ordinary temperature, after 3-hour neglect, rinsing desiccation was carried out and color contamination was observed.

Assessment judging O: Color contamination is completely nothing. \*\*: Color contamination is accepted slightly.

x: Color contamination is accepted.



## [0053] [Abrasion resistance test]

Equipment against which a version is ground while put the waste cloth of white knitted fabric on the friction part of the grinding equipment which can apply a load at the head of a testing device, a solvent is made to always permeate a waste cloth, and it is the same period and going.

\*\* \*\*\*\* heavy: -- 2kg/cm<sup>2</sup> grinding rate: -- 38 round trips / 60sec times number: -- 40,000 times stroke: -- 170mm assessment judging O: -- the trace of x:grinding that the trace of grinding is not observed is observed.

[0054] In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example 2 still pyridinium radical, block isocyanate (coronate 2513 made from Japanese Polyurethane Industry) 35g and vinyl acetate emulsion (product made from Hoechst Composition MA-206) 240g were mixed, the liquefied photopolymer constituent was created in them, and the version for screen-stencil was created and evaluated like the example 1 in them. The result is shown in a table 1.

[0055] The polyvinyl alcohol water solution which added the example 3 still pyridinium radical (polymerization degree 1700 and 88% of saponification degrees) To 100g of solid content, 12% Block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g, Vinyl acetate emulsion (Hoechst composition MA-206) 240g, As photopolymerization initiator diethyl thioxan ton ( KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g, and a polymerization promotor 7g emulsification and mixing of the acrylate oligomer ( TMPTA made from New Nakamura Chemistry) which carried out dissolution mixing of the 0.1g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds were done, the liquefied photopolymer constituent was created, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[0056] Block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g, vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g, and 5g of 10% diazo water solutions were mixed in 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example 4 still pyridinium radical, the liquefied photopolymer constituent was created, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[0057] In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example 5 still pyridinium radical, block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g, Vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g, As photopolymerization initiator diethyl thioxan ton ( KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g, and a polymerization promotor Acrylate oligomer ( TMPTA made from New Nakamura Chemistry) 7g which carried out dissolution mixing of the 0.1g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds was emulsified and mixed, and the liquefied photopolymer constituent was created. 5g of diazo water solutions was mixed 10% to the photopolymer constituent, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[0058] Block isocyanate (coronate 2507 made from Japanese polyurethane industry) 35g, vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g, and 5g of 10% diazo water solutions were mixed in 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example 6 still pyridinium radical, the liquefied photopolymer constituent was created, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[0059] 100g (water solution compounded in the example 3 of manufacture) of polyvinyl alcohol water solutions which added the example 7 still kino RIUMU radical -- block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g -- the place which was mixed and was stirred for 10 minutes by the homomixer -- the milk of thin yellow -- the white liquid (photopolymer constituent) was obtained. Using this liquefied photopolymer constituent, according to the conventional method of the version creation for screen-stencil, it applied to 150 meshes of polyester at the thickness of 15 micrometers, the positive film which drew the test pattern was stuck, and it exposed by distance 1M

with 4kw ultrahigh pressure mercury lamp, and when the spray of the water was carried out with the spray gun and the unexposed part was flushed, the test pattern image formed by the hardened film was obtained. This image (version) was put into hot blast oven, and 180 degrees C and heat-treatment for 90 minutes were performed. The version for screen-stencil after heat-treatment is evaluated, and the result is shown in a table 1.

[0060] Mixed emulsification of imino group mold BUTOOKISHI melamine (product M-508 made from Mitsui SAITEKKU) 28g which contains xylene 10g in 100g (polymerization degree 1700, 88% of saponification degrees, 12% of solid content) of polyvinyl alcohol water solutions which added the example 8 still pyridinium radical, and the vinyl acetate emulsion (Hoechst composition MA-206) 220g was carried out, the calcium-hydroxide saturated water solution adjusted to pH6.0, and the liquefied photopolymer constituent was created. The same approach as an example 1 created and estimated the version for screen-stencil using this liquefied photopolymer constituent. The result is shown in a table 1.

[0061] The polyvinyl alcohol water solution which added the example 9 photopolymer constituent still pyridinium radical (polymerization degree 1700 and 88% of saponification degrees) To 100g of solid content, 12% Block isocyanate (coronate 2507 made from Japanese Polyurethane Industry) 35g, Vinyl acetate emulsion (Hoechst composition MA-206) 240g, As photopolymerization initiator diethyl thioxan ton ( KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.25g, and a polymerization promotor 7g emulsification and mixing of the acrylate oligomer ( TMPTA made from New Nakamura Chemistry) which carried out dissolution mixing of the 0.2g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds were done, and the liquefied photopolymer constituent was created.

[0062] With the rotary screen printing above-mentioned liquid-like photopolymer constituent, it printed by creating the rotary screen version according to the following process.

(1) Wash and rinse the rotary screen cylinder-TS screen 125 (product [ made from Tree Sculpture ], and diameter 640mmphi, die length of 2,000mm, 125 meshes) manufactured by the emulsion spreading electroforming method with neutral detergent, and dry with 40-degree C hot air drying equipment. The dry cylinder was adjusted to installation and a ring-like bucket at the automatic spreading machine (Stoke AC-2000 mold), the above-mentioned photopolymer constituent was adjusted to the viscosity of 500cps / 25 degrees C, and 350g was supplied. It applied to upper part twist lower part by spreading time amount 16 minutes and 40 seconds / 1 time.

(2) \*\* The above-mentioned rotary screen cylinder which applied the \*\*\*\*\* constituent is looked like [ hot air drying equipment ] in the state of length, and 40 degrees C dries for 1 hour.

(3) Open The rotary screen cylinder which applied and dried the optical photopolymer constituent is put on an exposure machine. The film for images is twisted, a part for the connecting portion of a pattern is doubled, and it fixes with a Scotch tape (trademark). Succeedingly with an exposure machine (Stoke NEW-EP -2000) in 3kw metal halide lamp and the distance of 300mm Letting an exposure aperture pass and rotating the transit time 6 minutes and 30 second / 1 round trip of the light source, and a rotary screen cylinder 20 second / 10, it was made to go two times and exposed.

(4) \*\* Immediately after dipping an image rotary screen cylinder in a cistern for 3 minutes, after developing negatives with the developing machine (ADmade from Tree Sculpture- 2000) of a rotating type and an internal spray mold, a rotary screen cylinder is taken out, and with a water spray, the inside-and-outside section is washed, it carries out every length indoors, water is cut for 10 minutes, and it dries for 40 degrees C / 30 minutes with hot air drying equipment.

(5) The rotary screen cylinder was put into the hot blast circulation drying furnace heated by 40 degrees C of heat treatments, temperature up was carried out to 180 degrees C, and heat treatment was performed for 90 minutes at 180 degrees C.

(6) Mark The version was attached in \*\*\*\*\* and the cheesecloth was printed 10,000m.

Printing machine : rotary printing machine (R-200 by TOSHIN KOGYO CO., LTD. mold)

Printing ink: The emulsion paste containing reactive dye (seven sorts of seven colors)

Print : cheesecloth print speed : 50 m/min printing result is shown in a table 2. Consequently, even if the rotary screen version manufactured from the photopolymer constituent of elegance conventionally using

the dichromate of the present marketing and the printing result more than equivalent are obtained and it does not use dichromate, safety is high, and a photopolymer constituent without environmental destruction can be offered.

[0063] After rinsing the rotary screen cylinder after 10,000m printing of existence of ink stain resistance, it dried and the stain resistance of ink was observed.

O : there is no color contamination. x: Color contamination is accepted.

After rinsing the rotary screen cylinder after 10,000m printing of destructive of the photopolymer film of a version, it dried and wear of deemulsification and the edge section was observed. Wear was judged by whether the thickness of the rotary screen cylinder after printing is decreasing by measurement of thickness.

O : there are not deemulsification and wear. x: Deemulsification and wear are accepted.

The print at the time of 10,000m printing of blots of a printing image was observed.

O : the borderline of a color and a color has clarified.

x: The borderline of a color and a color does not clarify by blot.

It placed, and after rinsing the rotary screen cylinder after 10,000m printing of reuses of a version, it dried, 5,000m printing was performed again, and it observed about the existence of contamination of ink, and emulsion destruction of a version. The assessment approach is the same as the above.

[0064] Screen-stencil was created like the example 1 using the photopolymer constituent created by the same approach as example 10 example 3. Next, it irradiates, moving by conveyor which can carry out automatic migration while setting far-infrared irradiation equipment (far-infrared heater 500 with a general-purpose reflecting plate W 6, heater skin temperature of about 500 degrees C) to parallel for this version for Suku wood printing and keeping the distance of a far-infrared heater side and the version for screen-stencil at about 100mm. The skin temperature of the photopolymer constituent layer of the version for screen-stencil at that time is 180 degrees C. It irradiated for 3 minutes and passing speed 100 mm/min estimated the obtained version for screen-stencil according to the following approach. As the result was shown in a table 3, effectiveness equivalent to heat treatment by hot blast was acquired.

(1) It applied to the waterproof expansion test of the waterproof expansion test example 1 correspondingly, and carried out and evaluated.

(2) It applied to the abrasion resistant test of the abrasion resistant test example 1 correspondingly, and carried out and evaluated. A solvent uses water and TAPEN.

(3) It applied to the stain resistance trial of the ink of the existence example 1 of the stain resistance of ink correspondingly, and carried out and evaluated.

(4) Peel strength was measured for the bond strength of the screen pasted up on the frame and the adhesion-test version frame (construction material aluminum) of a screen with adhesives 180 degrees with S-autograph 500 mold by Shimadzu Corp., and discoloration of the adhesives at that time was observed.

[0065] 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example of comparison 1 still pyridinium radical was used as sensitization liquid, and the screen-stencil version was created and evaluated like the example 1. The result is shown in a table 1.

[0066] In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example of comparison 2 still pyridinium radical, vinyl acetate emulsion (MAmade from Hoechst Composition- 206) 240g was mixed, sensitization liquid was created in them, and the version for screen-stencil was created and evaluated like the example 1 in them. The result is shown in a table 1.

[0067] 7g emulsification and mixing of the acrylate oligomer (TMPTA made from New Nakamura Chemistry) which carried out dissolution mixing of the 0.1g (KAYACURE[ by Nippon Kayaku Co., Ltd. ] EPA) of the amine compounds at 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example of comparison 3 still pyridinium radical as photopolymerization initiator diethyl thioxan ton (KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g and a polymerization promotor are done, and it is [0068]. In 100g

(water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the example of comparison 4 still pyridinium radical, vinyl acetate emulsion (MA made from Hoechst Composition- 206) 240g and 10g of 10% diazo water solutions were mixed, sensitization liquid was created in them, and the version for screen-stencil was created and evaluated like the example 1 in them. The result is shown in a table 1.

[0069] In example of comparison 5 example 9, it carried out like the example 9 except having carried out using the sensitization liquid of a dichromate mold as sensitization liquid. The result is shown in a table 2.

[0070] In example of comparison 6 example 10, it carried out like the example 10 except having not processed far infrared rays. The result is shown in a table 3.

[0071]

[A table 1]

1

		実 験 成 果								比 較				例
		1	2	3	4	5	6	7	8	1	2	3	4	
分 散 媒	必須成分	100	100	100	100	100	100	100	100	100	100	100	100	
	任意成分				5	5	5						10	
分 散 質	架橋性化合物	36	36	36	36	36	35	35						
	任意成分								28					
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
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	任意成分		240	240	240	240	240	240	220		240		240	
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	任意成分		240	240	240	240	240	240	220		240		240	
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	任意成分		240	240	240	240	240	240	220		240		240	
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	任意成分		240	240	240	240	240	240	220		240		240	
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	任意成分		240	240	240	240	240	240	220		240		240	
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	任意成分		240	240	240	240	240	240	220		240		240	
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	任意成分		240	240	240	240	240	240	220		240		240	
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	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	35						
	任意成分		240	240	240	240	240	240	220		240		240	
評 価	架橋性化合物	36	36	36	36	36	35	3						

[0072]

[A table 2]

表 2

		実 施 例 9	比 較 例 5 従来品 (重クロム酸塩タイプ)
7色印刷後のインキ汚染性 (10,000m)		○	○
版の乳剤破壊		○	○
印刷物のしみ、汚染		○	○
置き版 の 再使用	インキ汚染性の有無 (5,000m)	○	○
	版の乳剤破壊	○	○

[0073]

[A table 3]

表 3

			実 施 例 10	比 較 例 6
遠赤外処理の有無			有	無
評 価	耐水膨潤率		5.3	39.0
	インキ汚染性		○	×
結 果	耐摩	水	○	×
	耗性	ターペン油	○	×

[Translation done.]

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WRITTEN AMENDMENT

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----- [procedure amendment]

[Filing Date] February 18, Heisei 12 (2000. 2.18)

[Procedure amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] 0006

[Method of Amendment] Modification

[Proposed Amendment]

[0006] That is, the photopolymer constituent of this invention is characterized by coming to distribute the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat into the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol %. The version for screen-stencil which is another invention of this invention It comes to form a resin layer in a screen mesh selectively. This resin layer It consists of that by which the water-insoluble nature particle over which the bridge was constructed by heat into the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out was distributed. And it is characterized by for the vinyl acetate polymer saponification object beyond saponification degree 50 mol % by which optical bridge formation was carried out with the water-insoluble nature particle over which the bridge was constructed by this heat constructing a bridge, and unifying it. The manufacture approach of the version for screen-stencil which is another further invention of this invention In the dispersion medium which consists of a water-soluble vinyl acetate polymer saponification object containing a styryl pyridinium radical or a styryl kino RIUMU radical beyond saponification degree 50 mol % After exposing after making a screen mesh apply and dry the photopolymer constituent which comes to distribute the dispersoid which consists of a cross-linking compound which constructs a bridge with water-insoluble nature or poorly soluble heat, and developing negatives, it is characterized by irradiating heating or a heat ray.

[Procedure amendment 2]

[Document to be Amended] Description

[Item(s) to be Amended] 0009

[Method of Amendment] Modification

[Proposed Amendment]

[0009] Vinyl acetate polymer

As a vinyl acetate polymer used for the vinyl acetate polymer saponification object beyond [ above-mentioned ] saponification degree 50 mol %, both the gay polymer of vinyl acetate and a copolymer are included. Specifically, it is the copolymer of polyvinyl acetate, vinyl acetate, this, and a copolymerizable monomer (comonomer). As vinyl acetate and a copolymerizable monomer, on a compound and a concrete target with ethylene or an ethylene nature partial saturation radical, for example Unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, a crotonic acid, a maleic acid, a fumaric



acid, and an itaconic acid Methyl acrylate, methyl methacrylate, 2-ethylhexyl acrylate, Acrylate, such as butyl acrylate; Acrylamide, methacrylamide, Acrylamides, such as N-methylol acrylamide, N, and N-dimethyl acrylamide; A vinyl chloride, Cationic monomers, such as vinyl compounds, such as a propylene, a butylene, and styrene, a dimethylaminoethyl meta-cleat, a vinyl imidazole, vinylpyridine, and vinyl SAKUSHIMIDO, can be mentioned. these compounds are independent -- or it can also be used together and used and, as for the content in the above-mentioned polymer, less than [ 30mol% ] is desirable.

[Procedure amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] 0034

[Method of Amendment] Modification

[Proposed Amendment]

[0034] (4) Business Way

Such a photopolymer constituent of this invention responds to various applications. Aluminum, It applies on the base material of arbitration, such as metal plates, such as nickel and stainless steel, a synthetic-resin plate and a semi-conductor substrate, and a stone. or [ drying and carrying out a laminating ] -- various screen mesh (a polyamide and polyester --) It applies to a table rear face or front faces, such as mesh, such as stainless steel, and a rotary screen cylinder. Into a photopolymer ingredient with a dry thickness of 1-1000 micrometers formed by drying The activity light which consists of ultraviolet rays etc. For example, after in the case of ultraviolet rays having irradiated through the predetermined pattern with the mask etc. so that the amount of exposure energy of the wavelength the range of 300-450nm might become two or more 10 mj/cm, and stiffening an exposure part, If spray water etc. removes the part which is not hardened [ of a non-irradiating part ], a relief image or the image film will be formed. Furthermore, about this formed relief image or image film, by carrying out exposure processing of heat-treatment or a near infrared ray, far infrared rays, the microwave, etc. in a 120-200-degree C ambient atmosphere preferably, the hardening reaction of the image film advances further and 50-220 degrees C becomes the image film excellent in a deck watertight luminaire and solvent resistance. Therefore, it can use for the application of resist film, such as the various printing versions which used such a photopolymer constituent, such as screen-stencil and Toppan Printing, and various etching resist, sandblasting etching, etc. It is desirable to use as a version for screen-stencil also in these applications.

[Procedure amendment 4]

[Document to be Amended] Description

[Item(s) to be Amended] 0055

[Method of Amendment] Modification

[Proposed Amendment]

[0055] Example 3

The polyvinyl alcohol water solution which added the still pyridinium radical (polymerization degree 1700 and 88% of saponification degrees) To 100g of solid content, 12% Block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g, Vinyl acetate emulsion (Hoechst composition MA-206) 240g, As photopolymerization initiator diethyl thioxan ton ( KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g, and a polymerization promotor Do 7g emulsification and mixing of the acrylate oligomer ( made from New Nakamura Chemistry "A-TMPT" (trimethylolpropane triacrylate)) which carried out dissolution mixing of the 0.1g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds, and a liquefied photopolymer constituent is created. The version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[Procedure amendment 5]

[Document to be Amended] Description

[Item(s) to be Amended] 0057

[Method of Amendment] Modification

[Proposed Amendment]

## [0057] Example 5

In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the still pyridinium radical, block isocyanate (coronate 2513 made from Japanese polyurethane industry) 35g, Vinyl acetate emulsion (MA made from Hoechst Composition- 206) 240g, As photopolymerization initiator diethyl thioxan ton ( KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g, and a polymerization promotor Acrylate oligomer ( made from New Nakamura Chemistry "A-TMPT" (trimethylolpropane triacrylate)) 7g which carried out dissolution mixing of the 0.1g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds was emulsified and mixed, and the liquefied photopolymer constituent was created. 5g of diazo water solutions was mixed 10% to the photopolymer constituent, and the version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[Procedure amendment 6]

[Document to be Amended] Description

[Item(s) to be Amended] 0061

[Method of Amendment] Modification

[Proposed Amendment]

## [0061] Example 9

Photopolymer constituent

The polyvinyl alcohol water solution which added the still pyridinium radical (polymerization degree 1700 and 88% of saponification degrees) To 100g of solid content, 12% Block isocyanate (coronate 2507 made from Japanese Polyurethane Industry) 35g, Vinyl acetate emulsion (Hoechst composition MA-206) 240g, As photopolymerization initiator diethyl thioxan ton ( KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.25g, and a polymerization promotor Acrylate oligomer ( made from New Nakamura Chemistry "A-TMPT" (trimethylolpropane triacrylate)) 7g which carried out dissolution mixing of the 0.2g (KAYACURE-EPA by Nippon Kayaku Co., Ltd.) of the amine compounds was emulsified and mixed, and the liquefied photopolymer constituent was created.

[Procedure amendment 7]

[Document to be Amended] Description

[Item(s) to be Amended] 0064

[Method of Amendment] Modification

[Proposed Amendment]

## [0064] Example 10

The version for screen-stencil was created like the example 1 using the photopolymer constituent created by the same approach as an example 3. Next, it irradiates, moving by conveyor which can carry out automatic migration while setting far-infrared irradiation equipment (far-infrared heater 500 with a general-purpose reflecting plate W 6, heater skin temperature of about 500 degrees C) to parallel for this version for screen-stencil and keeping the distance of a far-infrared heater side and the version for screen-stencil at about 100mm. The skin temperature of the photopolymer constituent layer of the version for screen-stencil at that time is 180 degrees C. It irradiated for 3 minutes and passing speed 100 mm/min estimated the obtained version for screen-stencil according to the following approach. As the result was shown in a table 3, effectiveness equivalent to heat treatment by hot blast was acquired.

## (1) A waterproof expansion test

It applied to the waterproof expansion test of an example 1 correspondingly, and carried out and evaluated.

## (2) Abrasion resistant test

It applied to the abrasion resistant test of an example 1 correspondingly, and carried out and evaluated. A solvent uses water and TAPEN.

## (3) Existence of the stain resistance of ink

It applied to the stain resistance trial of the ink of an example 1 correspondingly, and carried out and evaluated.

## (4) The adhesion test of a frame and a screen

Peel strength was measured for the bond strength of the screen pasted up on the version frame (construction material aluminum) with adhesives 180 degrees with S-autograph 500 mold by Shimadzu Corp., and discoloration of the adhesives at that time was observed.

[Procedure amendment 8]

[Document to be Amended] Description

[Item(s) to be Amended] 0067

[Method of Amendment] Modification

[Proposed Amendment]

[0067] The example 3 of a comparison

In 100g (water solution compounded in the example 1 of manufacture) of polyvinyl alcohol water solutions which added the still pyridinium radical, acrylate oligomer ( made from New Nakamura Chemistry "A-TMPT" (trimethylolpropane triacrylate)) 7g which carried out dissolution mixing of the 0.1g (KAYACURE[ by Nippon Kayaku Co., Ltd. ] EPA) of the amine compounds as photopolymerization initiator diethyl thioxan ton (KAYACURE[ by Nippon Kayaku Co., Ltd. ] DETX) 0.2g and a polymerization promotor was emulsified and mixed, and sensitization liquid was created. The version for screen-stencil was created and evaluated like the example 1. The result is shown in a table 1.

[Procedure amendment 9]

[Document to be Amended] Description

[Item(s) to be Amended] 0069

[Method of Amendment] Modification

[Proposed Amendment]

[0069] The example 5 of a comparison

It printed by using the dichromic acid emulsion with which elegance is marketed conventionally, and creating the rotary screen version like an example 9. A printing result is shown in a table 2.

[Procedure amendment 10]

[Document to be Amended] Description

[Item(s) to be Amended] 0071

[Method of Amendment] Modification

[Proposed Amendment]

[0071]

[A table 1]

実				施				例				比				較				例			
1	2	3	4	5	6	7	8	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
			5	5	5																		10
35	35	35	35	35	35	35																	
							28																
	240	240	240	240	240		220																240
		0.2		0.2																			
	0	0	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ
30	15	25	30	40	30	50	15	75	15	90	30	75	15	90	30	75	15	90	30	75	15	90	30
100	75	50	50	50	50	120	75	200	100	150	50	200	100	150	50	200	100	150	50	200	100	150	50
4	6.0	5.4	5.5	5.2	6.4	7.8	3.8	55.8	40.5	48.5	8.7	55.8	40.5	48.5	8.7	55.8	40.5	48.5	8.7	55.8	40.5	48.5	8.7
	0	0	0	0	0	0	0	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
	0	0	0	0	0	0	0	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x

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